COPPER IN THE SEA: A PHYSICAL-CHEMICAL STUDY OF RESERVOIRS, FLUXES AND PATHWAYS IN AN ALASKAN FJORD

A

DISSERTATION

Presented to the Faculty of the

University of Alaska in Partial Fulfillment

of the Requirements

for the Degree of

DOCTOR OF PHILOSOPHY

By

David Thomas Heggie - B.Sc., M.Sc.

Fairbanks, Alaska

December 1977

COPPER IN THE SEA: A PHYSICAL-CHEMICAL STUDY OF

RESERVOIRS, FLUXES AND PATHWAYS IN AN ALASKAN FJORD

RECOMMENDED:

_____

_____

_____

_____

_____

_____

Chairman, Advisory Committee

_____

Program Head

APPROVED:

_____

Dean of the College of Environmental Sciences

_____

Date

_____

Vice Chancellor for Research and Advanced Study

_____

Date

ABSTRACT

Copper in the sea is derived principally from continental weathered products added to the oceans at continental boundaries, hence processes, fluxes and pathways in estuaries control the supply of copper to the marine biosphere. From mass balances, the fluxes, sources and sinks of copper in an Alaskan fjord were examined by utilizing fjord deep waters as an approximation to a closed chemical system. Copper was measured in the water columns and interstitial waters electroanalytically with a precision of 10%. Concentrations of 'soluble' copper ranged between 0.14 μg ℓ^{-1} and 3.13 μg ℓ^{-1} (mean = 0.50 μg ℓ^{-1}). Approximately 40% of 'total' copper was associated with particulate matter in the water column. Concentrations of copper in interstitial waters varied between 1.02 and 9.98 μg ℓ^{-1}; maximum concentrations were always found in surface segments. Concentrations of copper on sediments were about 20 mg kg^{-1}. Copper was removed from the water column and transported to the sediments by particulate matter; net annual removal was estimated to be between 9.6 and 14.2 μg Cu cm^{-2}. Copper was remobilized from the solid phase(s) in surface sediments and subsequently returned to the overlying water; net annual transport across the sediment-seawater interface was estimated to be 1.9 μg Cu cm^{-2}. Therefore, between 13 and 20% of copper removed from the water column to the sediments was returned to the water column. Remobilized copper not returned to the water column was removed from interstitial waters in the anoxic zone of sediments. Remobilization and removal processes in sediments

take place in thin ∿ 10 cm zones and effective rates of reactions in sediments may be one to three orders of magnitude greater than reaction rates in the water column. A hypothesis is presented for transport of copper to the sediments predominately on biogenic particles.

ACKNOWLEDGEMENTS

This research was supported by the Energy Research and Development Administration under contract number E(45-1)-229, TA No. 1.

I wish to thank David Burrell for the opportunity to work on this contract, his friendship and support to the termination of this work. A mention in acknowledgement is insufficient to express the gratitude that I owe to my friend Tina for her companionship and support through the more difficult years of this work. My associations with Bill Reeburgh (chemical oceanography) and Tom Royer (physical oceanography) have been important for my education. Dan Hawkins, Ray Hadley and Dave Musgrave read and commented upon an early version of this manuscript.

I would like to thank the following persons for their assistance and/or cooperation during several and various aspects of this work: E. R. Dieter (shipboard operations), D. Boisseau (shipboard operations), R. Ashley (engineer R/V *Acona*), K. Turner (master R/V *Acona*), J. Bradbury (glassblower), G. Gislason (mathematics), R. Hobson (computer programming), Ana Lea Vincent and Judith Henshaw (drafting), and students and technicians in Dr. Burrell's laboratory, M. L. Lee, Ray Hadley and Tom Manson. I appreciate the efforts and assistance of Suzette Carlson and Helen Stockholm in the seemingly endless task of typing and editing the manuscript.

COPPER IN THE SEA: A PHYSICAL-CHEMICAL STUDY OF RESERVOIRS, FLUXES AND PATHWAYS IN AN ALASKAN FJORD

David Thomas Heggie, Ph.D.

University of Alaska, 1977

Supervisor: David C. Burrell

Copper in the sea is derived principally from continental weathered products added to the oceans at continental boundaries, hence processes, fluxes and pathways in estuaries control the supply of copper to the marine biosphere. From mass balances, the fluxes, sources and sinks of copper in an Alaskan fjord were examined by utilizing fjord deep waters as an approximation to a closed chemical system. Copper was measured in the water columns and interstitial waters electroanalytically with a precision of 10%. Concentrations of 'soluble' copper ranged between 0.14 μg ℓ^{-1} and 3.13 μg ℓ^{-1} (mean = 0.50 μg ℓ^{-1}). Approximately 40% of 'total' copper was associated with particulate matter in the water column. Concentrations of copper in interstitial waters varied between 1.02 and 9.98 μg ℓ^{-1}; maximum concentrations were always found in surface segments. Concentrations of copper on sediments were about 20 mg kg^{-1}. Copper was removed from the water column and transported to the sediments by particulate matter; net annual removal was estimated to be between 9.6 and 14.2 μg Cu cm^{-2}. Copper was remobilized from the solid phase(s) in surface sediments and subsequently returned to the

overlying water; net annual transport across the sediment-seawater interface was estimated to be 1.9 μg Cu cm^{-2}. Therefore, between 13 and 20% of copper removed from the water column to the sediments was returned to the water column. Remobilized copper not returned to the water column was removed from interstitial waters in the anoxic zone of sediments. Remobilization and removal processes in sediments take place in thin ∿ 10 cm zones and effective rates of reactions in sediments may be one to three orders of magnitude greater than reaction rates in the water column. A hypothesis is presented for transport of copper to the sediments predominately on biogenic particles.

TABLE OF CONTENTS

CHAPTER PAGE

LIST OF FIGURES

LIST OF APPENDIX FIGURES

APPENDIX A

APPENDIX B

APPENDIX C

LIST OF TABLES

TABLE PAGE

LIST OF APPENDIX TABLES

APPENDIX C

I. COPPER IN THE SEA: AN INTRODUCTION

Marine trace metal geochemistry research currently is focused upon two distinct but complementary topics:

i. chemical speciation and the effect of different complex forms of metals on reactions at abiotic and biological particle surfaces and upon marine photosynthesis and growth, and

ii. spatial and temporal element distributions in oceanic and estuarine environments.

This dissertation is concerned with the latter, and specifically, the behavior of copper in seawater. Non-conservative behavior is examined, fluxes are computed and reservoirs elucidated as sources and/or sinks. Brief presentations of the biological importance of and the chemistry of copper in the sea precede a discussion of marine geochemical reservoirs fluxes and routes of copper. The reasons why progress in this area of trace metal geochemistry has been slow are stated. The focus of this work and the approach to be adopted are then presented.

Copper is ubiquitous in the oceanic domain, being dissolved in seawater and concentrated in plants and animals, suspended abiotic particles, sediments and the puzzling manganese nodules which cover large areas of the ocean floor. Copper in the biosphere and hydrosphere and oceanic sediments constitutes only about 2% (biosphere and hydrosphere <1%) of the total global copper budget (Rickard, 1970; Table 1). However, it is this 2%, *via* diverse inorganic/organic chemical and biological cycling and throughput reactions that is fundamental to the existence and maintenance of life in the oceans.

TABLE 1

Estimates of Average Copper Concentration and Mass in Various Geochemical Units (Rickard, 1970).

	Mass of X 10^{15} tons.[1]	Mean copper concentration ppb	Mass of copper X 10^{10} tons.
Oceanic Rocks			
Sediments	217	140000[2a]	3000
Mafic rocks	4400	80000[2]	38300
Sedimentary Rocks			
Sandstone	280	100[2]	3
Shales	750	45000[2]	3375
Limestones	290	4000[2]	116
Evaporites	30	20000[4]	6
Subsurface waters	201	20[5]	0.4
Fresh water	0.3	7[3]	0.00021
Sea water	1420	2[6]	0.28
Atmospheric water	0.5	1[3a]	0.000036
Ice	35	1[7]	0.0035
Continental Igneous and Metamorphic Rocks			
Granitic	10500	30000[2]	31500
Mafic	8700	87000[2]	75700
Living and undecayed organic matter	0.004	20000[8]	0.008

[1] Modified from Poldervaart (1955) and Holser and Kaplan (1966), except data for mass of atmospheric water modified from Turekian (1969).

[2] Estimated after Parker (1963); [2a] assuming siliceous/carbonate ratio = 1 (Wedepohl, 1969).

[3] Turekian (1969); [3a] Sugawara (1967).

[4] Estimated after Stewart (1963).

[5] Estimated from data in White *et al.*, (1963) and this text.

[6] Estimated from this text.

[7] Estimated from data on copper content of fresh, atmospheric and ocean water in this text.

[8] Estimated from data in this text.

Biological Importance

The biological importance of copper in the sea has been reviewed by Lewis and Whitfield (1974). Copper plays a dual role in life sustaining processes in the sea. It is an 'essential' requirement of plants and animals but may be toxic at elevated concentrations. Life in the oceans is limited by primary productivity. The effect of copper on photosynthesis and growth has been examined for the green algae *Chlorella pyrenoidosa* (Steemann-Nielsen *et al.*, 1969) and the diatom, *Nitzschia palea* (Steemann-Neilsen and Wium Anderson, 1971). Copper was deleterious to growth and photosynthesis in both organisms, but the toxic effect on the diatom seemed to be removed by the excretion of organic matter.

The relatively low growth observed in freshly upwelled deep ocean water is to be contrasted to the high growth observed in 'aged' upwelled water. The former is believed to be due to, although light and nutrients were readily available, a lack of an association between trace metals (copper included) and organic matter (Barber and Ryther, 1969; Steemann-Nielsen and Wium Anderson, 1970; Barber *et al.*, 1971).

Natural Water Chemistry of Copper: A Brief Review

For all metals, except possibly sodium, the amount added to the sea *via* weathering and continental runoff exceeds that actually found (Goldschmidt, 1932 geochemical balance cited Krauskopf, 1956). Goldschmidt (1937) and Goldberg (1954) suggested that the rare metal concentrations, including copper, were kept low by adsorption onto particle

surfaces. Krauskopf (1956) reviewed this problem, and showed through calculation and experiment that the concentration of copper in equilibrium with the most likely least soluble copper compound in seawater (copper carbonate) exceeded the actual, then measured, concentrations in seawater by factors of from 30 to 800. Krauskopf (1956) demonstrated experimentally that copper could be effectively adsorbed onto the surfaces of iron and manganese oxides, apatite, clay and plankton.

A measure of the relative reactivity of an element in the ocean is residence time: the time that the element spends in the ocean before it is permanently lost to the sediments. The most reactive elements have short residence times and, in this respect copper would be classified as 'intermediate' in reactivity with a residence times in the ocean of between 2 and 5 x 10^4 years (Brewer, 1975). The present day oceanic dissolved copper concentration, in the probable absence of control by precipitation equilibria, is apparently controlled by a balance between rates of supply from continental runoff and rates of removal onto particulate surfaces. The relative reactivity of copper, because of the apparent undersaturation, is a reflection of incorporation either into or onto particles. The chemical nature of the dissolved state is suspected of being responsible for many trace metal reactions in the sea and elucidation of the above has been approached theoretically and experimentally.

Theoretical Equilibrium Models

The chemistry of copper in aqueous solutions is characterized by an ability to enter into complex formation with both inorganic and

organic species. The analysis of the distribution of a metal ion between various competing complexing ligands in seawater requires a knowledge of the activities of the ligands and the metal ion, and the formation constants of the possible association products. An incomplete knowledge of activity coefficients and formation constants has, however, led to discrepancies between various seawater inorganic speciation models of the relative distributions of various metal-ligand species (Zirino and Yamamoto, 1972; Dyrssen and Wedborg, 1974; Stumm and Brauner, 1975; Morgan and Sibley, 1975). Equilibrium models incorporating organic ligands suffer from an added uncertainty; the unknown nature, and concentrations of ligands of organic matter in seawater. The use of chemical analogs of probable organic ligands in seawater has indicated that, although much less abundant ($<10^5$) than the inorganic ligands, some organic ligands are effective in complexing with copper (Stumm and Morgan, 1970; Stumm and Brauner, 1975). Models of these types have been extended to include:

i. the redistribution of chemical species when seawater and sewage outfall water are mixed (Morgan and Sibley, 1975);

ii. examination of the dominant species in a freshwater model including adsorption (treated as a complexing ligand) onto a silica dioxide surface, and the redistribution of the chemical species when the above freshwater was mixed with seawater (Sibley and Morgan, 1975); and,

iii. a theory of chelator-metal ion interaction and phytoplankton growth (Jackson and Morgan, 1975).

Gardner (1974) has evaluated the relative importance of organic versus inorganic complexes in sulfide containing waters (characteristic

of many marine sediments) and found that for copper, and many of the trace metals, bisulfide and polysulfide complexes were dominant. Complexation by relatively simple organic ligands was not important but the effects of highly polymerized substances such as humic acids could not be accounted for.

Models of these types are equilibrium models and interpretation of the results must be constrained by kinetic factors, especially in estuarine environments. Nevertheless, they are useful in that they predict the relative distributions of various species at equilibrium - the direction chemical systems drive thermodynamically.

Experimental Speciation Studies

The acceptance or rejection of predictions of species distributions from model calculations has been slow but recent advances in experimental techniques have provided some solutions to the previously mentioned problems. Shuman and Woodward (1973) described a method for the determination of apparent formation constants of metal-organic ligand species in natural waters, and Lee (personal communication) has, *via* pH and pCl titrations combined with anodic stripping voltammetry, examined the importances of hydroxo and chloro copper complexes in solutions approximating the ionic strength of seawater. Stability constants determined for these species when applied to an inorganic seawater model indicated that copper appeared predominately as a copper chloride complex ($CuCl_4^{2-}$). Vuceta (1976) examined the adsorption

of copper on α-quartz and found the adsorption to be diminished by the presence of copper complexing ligands such as citrate and EDTA. O'Connor and Kester (1975) studied the adsorption of copper onto illite and found it to be reduced by increased solution ionic strength, concentrations of complex forming ligands with copper and by magnesium ions, the latter apparently compete with copper for adsorption sites on the solid surface.

Oceanic Reservoirs

Copper enters the ocean principally *via* continental weathering and runoff (Table 2). Input from deep ocean hydrothermal sources (except in localized areas) appears generally to be unimportant (Boström *et al.*, 1975; Bender and Gagner, 1976). Within the oceanic domain copper apparently interacts with the many particle types to be transported down and removed from the oceanic mixing cycle when buried and locked into the sediments. Copper is enriched in deep sea sediments; but concentrations cannot be explained by equal mixtures of the continental source rocks (granite and basalt) that constitute the dominant source material for the sediments (Broecker, 1974; Table 4-2). The elucidation of sources of some other metals in sediments - lead (Chow and Patterson, 1962); uranium (Ku and Broecker, 1969; Veeh and Boström, 1971) - has been accomplished by measurement and comparison of isotopic ratios of the elements in sediments with other reservoirs, but this has not been done for copper. From input through removal, little is known of the journey that copper takes through the ocean. Figure 1,

Table 2

2a. Copper Transport in the Amazon and Yukon Rivers (Gibbs 1973)

Mechanism	Amazon River (Percent of Total)	Yukon Rivers (Percent of Total)
In solution and organic complexes	6.9	3.3
Adsorbed	4.9	2.3
Precipitated and coprecipitated	8.1	3.8
In organic solids	5.8	3.3
In crystalline sediments	74.3	87.5

2b. Annual Discharge of Copper to the World's Ocean (Goldberg 1975)

Mechanism	Discharge (10^7 kg yr^{-1})
In solution and organic complexes	6.1
Adsorbed	22
Precipitated or coprecipitated	36
In organic solids	28
In crystalline sediments	540
Approximately	630

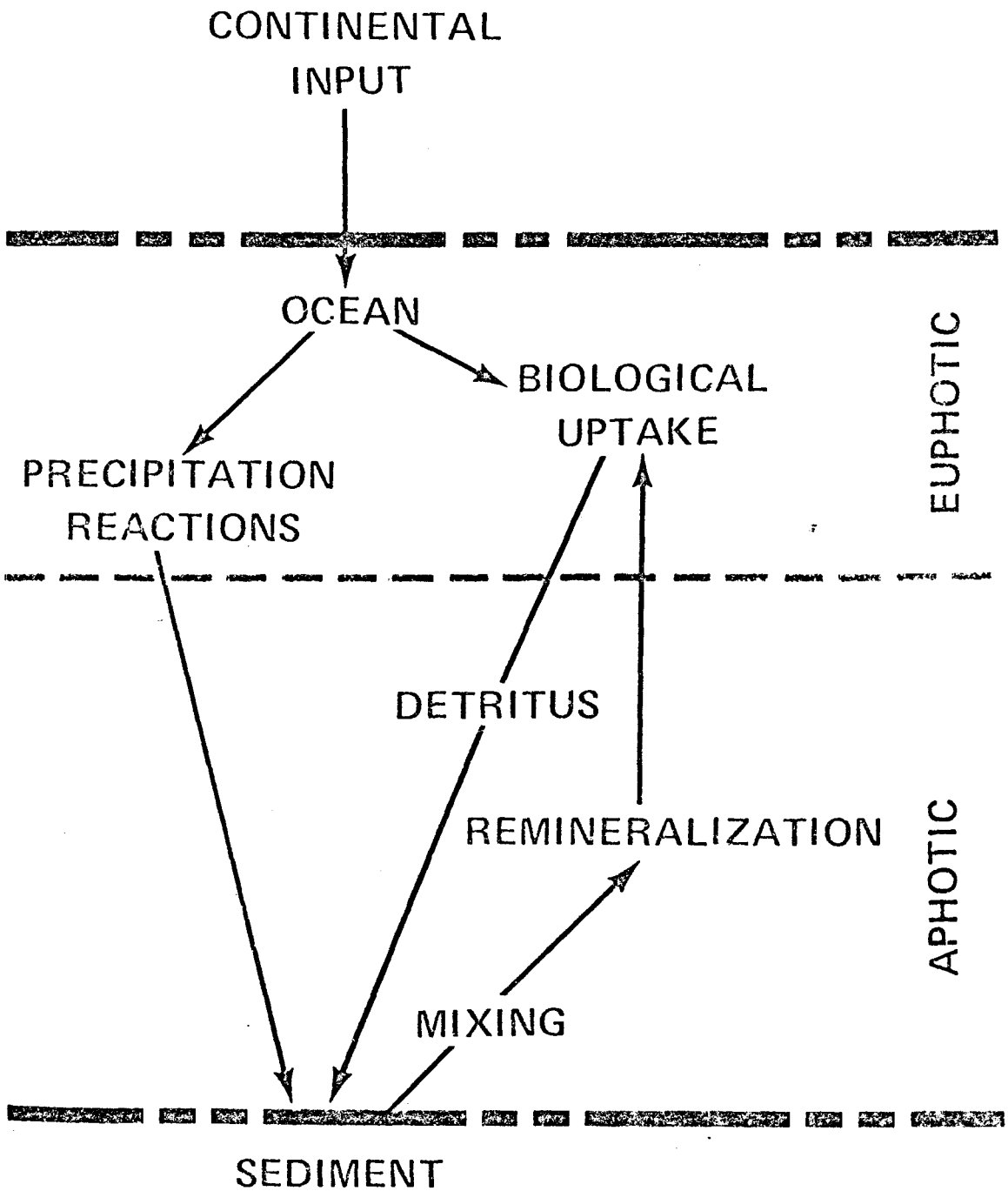


Figure 1. Idealized diagram of copper cycles in the sea (adapted from Lewis and Whitfield, 1974).

adapted from Lewis and Whitfield (1974), illustrates what is thought about the copper cycle in the sea and about represents the current state of knowledge. Diagrams of this nature are composites of data from various sources, mostly bulk analyses of various reservoirs, such as continental weathering products (Gibbs, 1973), suspended oceanic particles (Martin and Knauer, 1973; Martin, 1970), oceanic sediments (Goldberg and Arrhenius, 1958), and other data that indicate undersaturation and particle associations (Goldberg, 1954; Krauskopf, 1956).

Concentrations of Copper in Sea and Interstitial Waters

Some published measurements of copper in seawater are summarized in Table 3. Advances in instrumentation and an increased awareness of contamination problems associated with the collection, treatment and measurement of samples for trace metals has resulted in, about a decade, a lowering of the accepted level of copper in seawater from about 3 $\mu g\ \ell^{-1}$ (Goldberg, 1965) to about 0.5 $\mu g\ \ell^{-1}$ (Brewer, 1975). The data shown in Table 3, have been obtained for various reasons and with a variety of analytical techniques. Some studies have examined the distribution of copper between various 'fractions', others have examined seasonal variations and still others represent isolated measurements in various parts of the worlds oceans. They reflect the still exploratory nature of trace metal studies in general. Nevertheless, data such as these and others have contributed to the idealized diagram of copper cycles in the sea shown in Figure 1.

Table 3

Selected Studies of Copper Concentrations in Seawater

Area	Concentration $\mu g\ \ell^{-1}$	Reference
San Juan channel Washington	1.02 - 2.05	Chow and Thompson, 1954
Florida coastal	<20 (T)* < 2 (I) ∿ 0.2 (P)	Alexander and Corcoran, 1967
Gulf of Maine	0.5 - 21.3	Spencer and Brewer, 1969
Sargasso Sea	0.1 - 4.7	
N.E. Pacific Ocean	0.5 - 4.1(F) 0.4 - 2.7(U)†	Spencer *et al.*, 1970
Black Sea	0.3 - 8.0	Spencer and Brewer, 1971
Gulf of Mexico	0.10- 12.3 (T)‡ 0.04- 8.0 (E)	Slowey & Hood, 1971
U.K. Coastal	0.9 - 4.74	Abdullah *et al.*, 1972
British Isles	0.7 - 2.8	Preston *et al.*, 1972
Irish Sea	0.9 - 3.1	
Sargasso Sea	0.40- 7.90	Brewer *et al.*, 1972
S.W. Pacific Ocean	0.06- 0.20	Boyle and Edmond, 1975a
Sargasso Sea		
Surface	∿0.12	Bender and Gagner, 1976
Deep	∿0.15	

† F = Filtered
U = Unfiltered

* T = Total soluble
I = Ionic
P = Particulate

‡ T = Total
E = Extractable

Copper measurements in pore fluids squeezed from sediments are much fewer in number than those in the water column, and published concentration data are summarized in Table 4: concentrations vary over about three orders of magnitude. These works appeared to be of an observational and exploratory nature, stimulated by interest in the formation of authigenic minerals, to examine the reactions and the processes that metals undergo during early diagenesis. Two generalizations pertinent to this dissertation can be made about trace metals, specifically copper, in interstitial fliuds.

1. Concentrations are enriched over normal seawater values. Recent works (Callender, 1976; Krom, 1976) report enrichment of copper in interstitial waters about one order of magnitude higher than overlying waters.

2. Concentrations in anoxic pore waters, containing hydrogen sulfide, are not in equilibrium with solid sulfide phases.

Geochemical Fluxes

Estuaries are believed to play an important role in controlling the fluxes of continentally derived material to the deep ocean. The former appear to be sinks for some elements e.g., iron, (Coonley *et al.*, 1971; Boyle *et al.*, 1975) and lead (Benninger *et al.*, 1975). However, Evans and Cutshall (1972), found partial desorption of Zn^{65} and Mn^{54} from suspended particulate matter during estuarine mixing, but Zn^{65}, Mn^{54}, Cr^{51}, Se^{46}, and Sb^{124} showed no evidence of removal from solution as a result of flocculation, precipitation or adsorption consequent to estuarine mixing. Kharkhar *et al.* (1968) predicted from laboratory

Table 4

Reported Concentrations of Copper in Interstitial Waters

Area	Concentration $\mu g\ \ell^{-1}$	Reference
Southern California basins	0.9 - 16.0	Brooks *et al.*, 1968
Saanich Inlet British Columbia	0.5 - 39.0	Presley *et al.*, 1972
Loch Fyne Scotland	4 -380	Duchart *et al.*, 1973

studies that the soluble contents of Ag, Se, Co, but not Mo in oceanic waters were increased by desorption from river borne particulates. DeGroot (1966) and DeGroot *et al.* (1969) (cited in Martin *et al.*, 1970) found that Cs^{137}, Pb, Cu, and Fe were desorbed when freshwater and marine water were mixed. However Ra, Mn, Mo, and Sm remained unchanged (DeGroot *et al.* 1969; Clanton, 1963; cited in Martin *et al.*, 1970). Boyle *et al.* (1975) found that silica was conservative when river waters and oceanic waters mixed in estuaries. The cited studies suggest estuaries act as both sources and sinks for some elements but simply as 'conveyor belts' to transport other elements to continental shelf and deep ocean waters.

Estuarine Mixing Models

Attempts to resolve the above for different elements and to compute fluxes through estuaries have usually involved estuarine mixing models. The approach, applied to the relatively shallow depths of mixing zones of fresh and salt water in estuaries where horizontal advection and entrainment flow dominate the water transport processes, requires definition of the mixing end members, i.e., riverine and oceanic concentrations. A demonstration of non-conservative behavior when river water is mixed with oceanic water is reflected in a departure from linearity between the mixing end members. In addition to the difficulties associated with collecting and measuring the extremely low concentrations of trace metals in natural waters, the successful

application of this approach to an examination of non-conservative behavior of trace metals appeared doubtful for the following reasons.

1. The simplest model requires single valued end member concentrations. Freshwater runoff into estuaries varies seasonally, may show marked diurnal variations, and elemental concentrations may vary with flow conditions. Similarly, continental shelf source water variations might be such that measurements made at any particular time might not be representative of estuarine resident water.

2. To define and sample within a 'mixing zone' between any two 'oceanic' and 'riverine' end members, both of which may vary in time, presents a difficult resolution and sampling problem. Alternatively, examination of average values of variations of mixing end members and estuarine data over a time period sufficient to filter out short term variations increases the uncertaintity associated with delineating non-conservative behavior, and requires sampling through space and time that would be impractical.

3. The time scale of any reaction of interest upon mixing of end members has to be rapid with respect to the mixing time to delineate non-conservative behavior.

Some of these problems have led to ambiguities about non-conservative behavior of some other elements. Boyle *et al.* (1975), demonstrated that apparent non-conservative behavior of silica in some previous studies was the result of incomplete definition of mixing end members.

Uncertainties have arisen in models of these types even though well defined and precise analytical techniques were available for

elements that exist in the oceans at concentration levels about two orders of magnitude greater than most trace metals. Windom *et al.* (1971; cited in Boyle 1975) were apparently unable to demonstrate non-conservative behavior for Cu, Ni, and Zn in three south-east U.S. estuaries.

Deep Water Mixing Models

The problem of delineating non-conservative behavior from transport effects may be alleviated somewhat by examining depth distributions of chemical species of interest. Time scale characteristics of advection and mixing in the vertical are about three orders of magnitude less than those in the horizontal plane. This means that concentration differences, and hence chemical gradients, which result from reactions in the water column and/or exchange across boundaries, are relatively preserved through time. Horizontal transport, however, may confuse the interpretation of vertical profiles and needs to be carefully evaluated. Select regions of the oceans, however, have been found where 'mixing intervals', confined to a vertical direction only, have been defined. The north-east tropical Pacific Ocean is one such place where Craig (1969; 1974) has described the distributions of and computed fluxes of respectively carbon and copper with a one-dimensional vertical advection-diffusion model between about one and four kilometers depth. Similarly, Spencer and Brewer (1971) computed fluxes of dissolved and particulate manganese across a redox discontinuity in the Black Sea. The approach in these models is to fit the vertical profile

of the element of interest first with a conservative mixing model. Non-conservative behavior is evaluated by examining statistically any improvement to the fit, when a non-conservative consumption or production term is included in the mixing equation. Craig *et al.* (1973) have demonstrated that if a naturally occurring radioactive isotope exists for a trace metal, that disequilibrium between it and the parent isotope may be used as a quantitative measure of non-conservative behavior. From measurements of lead-210 and radium-226 Craig *et al.* (1973) found lead to be scavenged from the deep waters of the Pacific and Atlantic Oceans. Copper, however, has no such naturally occurring radio-isotope and any examination of non-conservative behavior requires precise measurements of naturally occurring stable copper.

Deep oceanic environments of the types mentioned are ideal to examine distributions and compute fluxes: the justifiable assumption of steady state conditions greatly simplifies solutions to the property-mixing-equations. Steady state conditions do not hold however in estuaries where marked seasonal variations in terrestrial and *in situ* particle fluxes and circulation patterns occur: all of these exert some control over trace metal concentrations. The non-steady state conditions also impart severe analytical restraints over and above those required in deep sea studies, where a single profile in time only is required.

If non-conservative behavior is to be evaluated and fluxes computed in estuarine environments, measurements have to be made through real time with a precision sufficient to distinguish small concentration changes.

The Problem

From the foregoing discussion several facts about the geochemistry of copper in the sea may be stated. These facts reflect the diversity of reactions and pathways that copper participates in and imply the cycling of copper between reservoirs. The data collected and the discussion in this work will focus upon the following points.

1. Copper enters the ocean primarily on continental weathered products with freshwater runoff. For a steady state oceanic copper concentration, rates of supply are balanced by rates of removal. Fluxes of copper to the deep ocean are apparently determined by reactions at continental boundaries. However, the delineation of non-conservative behavior from physical transport processes in estuaries has not been accomplished from measurements of copper dissolved in seawater. There is no *a priori* reason to suppose that fluxes of copper through oceanic and estuarine environments are equivalent, but little is known of either.

2. Copper is dissolved in seawater, but is relatively more concentrated in marine biota, inorganic particles and sediments. The relative importances of net supply to, versus net removal from, different reservoirs are not known: i.e., fluxes and directions of transfer, hence elucidation of sources and sinks.

3. Sediments are believed to be the ultimate sink of copper in the sea, but measurements of copper in sediment pore fluids have shown the latter to be concentrated over normal seawater copper values

by up to several orders of magnitude. Therefore, sediments must be considered a potential source of metals for the overlying water. Little is known of the role pore fluids play in the overall copper economy.

The above questions exist because of difficulties associated with the collection and measurement of seawater samples containing extremely low metal concentrations and because the ocean is in constant motion. The effects of physical transport phenomena have to be resolved from chemical and biological effects to delineate non-conservative behavior, compute fluxes and define sources and sinks. Two specific reasons may be stated.

1. Recent measurements of copper in the sea suggest that historical measurements are suspect. Relative differences in concentrations may be used to define reservoirs, but the computation of fluxes depends upon precise and accurate values.

2. Estuarine mixing models of the type used to examine non-conservative behavior at the micromolar level do not appear an attractive means of delineating non-conservative behavior at the nanomolar level. Observations in a vertical plane, because of the relative preservation in time of concentration differences, offer an alternative. However, steady state vertical mixing-models used elsewhere are not applicable to the time and length scales of processes operating in estuaries.

Precise analytical data, combined with close hydrographic controls, are required to resolve non-conservative behavior from transport effects in estuarine areas.

The Approach

Fjords with sills and enclosed deep basins often provide ideal environments to study geochemical processes. Horizontal advective exchanges with adjacent coastal water may be limited to discrete times of year, and between these, effects of chemical changes and input or export across boundaries are preserved in the water column. The intent of this work is to use the water column of one deep fjord basin as a 'geochemical bucket'. The analogy of a deep fjord basin, below sill depth, to a 'bucket' is not difficult to envisage. If Recent sediments are included, the 'geochemical bucket' approximates a closed chemical system. Matter and energy are transported into/out of the system only across the upper boundary (sill depth contour), and when these are accounted for, a mass balance for copper in the basin may be examined. From precise measurements of copper in the water column and interstitial waters, non-conservative behavior may be examined after accounting for mixing and advective transports into/out of the basin. Concentration changes and gradient growth and decay through real time are to be used to compute fluxes and to examine sources and sinks.

A two-year examination of the hydrographic characteristics of some Alaskan fjords indicated that only Resurrection Bay (described in Chapter 2), could be sampled at the desired frequency in time to adequately describe the deep water exchange processes. Hence, this fjord was chosen as the site for the present study.

Dissertation Outline

This dissertation presents the seasonal variations of copper concentrations in the water column and interstitial waters of Resurrection Bay which have been made with a sensitive electrochemical (differential pulsed anodic stripping voltammetry DPASV) technique. The work was designed to:

i. investigate non-conservative behavior of copper in a fjord estuary,

ii. compute fluxes of copper between different reservoirs within the fjord,

iii. elucidate the sources and sinks of copper in the fjord,

iv. define pathways responsible for the transport between the sources and sinks.

The second chapter describes the general hydrographic features of Resurrection Bay, but emphasizes the frequency and extent of deep water exchange of the inner basin with adjacent coastal water. Salt and heat budgets are used to compute volumes of water involved in the exchange and coefficients of eddy mixing across the sill depth. The application of these types of data to non-conservative elements is demonstrated through an examination of seasonal oxygen distributions. Chapter three discusses differential pulsed anodic stripping voltammetry with respect to measurements of copper in seawater.

Chapter four describes the seasonal variations of copper in the water column and interstitial waters of the fjord. The effects of the circulation on these data are discussed, and the parameters derived from chapter two are used to resolve advective and mixing effects

from copper distributions. Processes, fluxes, sources and sinks are examined from mass balances. Pathways responsible for the transport are postulated.

The final chapter presents conclusions and some thoughts for future studies that were generated from the results of this work.

II. THE EXCHANGE OF DEEP WATER BETWEEN THE GULF OF ALASKA AND RESURRECTION BAY.

INTRODUCTION

The use of deep fjord basins as 'geochemical buckets' requires a quantitative knowledge of the frequency and extent of deep and bottom water renewals. The resolution of non-conservative behavior and the computation of geochemical fluxes demand that these be known. A brief survey of deep water exchanges in some other fjords preceeds a quantitative examination, utilizing hydrographic observations over about a three year period (1972-1975) and a series of current meter measurements in 1973, of the deep water exchange between Resurrection Bay and the Gulf of Alaska.

Circulation in Fjord Basins

Fjords are characterized morphologically by steep sides, deep basins and a sill that inhibits the direct exchange of fjord water with adjoining marine coastal water. Surface circulations generally are determined directly by the relative importances of river runoff, tidal action and external forces such as winds. However, deep water circulation patterns generally are determined by processes that cause the density of the adjacent marine source water to vary and to be advected across a sill, and by *in situ* processes such as thermohaline convection and turbulent exchange. Nebert (1972) in Endicott Arm and Reeburgh *et al.* (1976), in Russell Fjord, found almost continuous, apparently tidal-driven additions to the deep waters across the sills

of these Alaskan fjords. Major bottom water renewal apparently could occur at any time of the year in Endicott Arm, but in Russell Fjord (Reeburgh *et al.*, 1976), the bottom water renewal occurred principally only during the spring when the density of the near surface waters beyond the sill were at their seasonal maximum. Successive replacement of the deep water, but at shallower depths, occurred year round however and in a three month (July-September) period of 1973 approximately 25% of the fjord basin water was replaced. "Bolus" type additions of water across a sill have been postulated for Saanich Inlet (Vancouver Is., Canada) by Anderson and Devol (1973). The deep water renewal appeared to take place annually but only in the fall months of August through October when the density of water at the sill, formed by the mixing of upwelled water off the Washington coast with warmer Georgia Strait water in Puget Sound, was a maximum. Cannon (1973) measured currents on the sill of Port Susan in Puget Sound and also found deep water renewal to take place during the fall months. Inflow, which occurred continuously over approximately five day periods, was however not related to the tides. Gade (1970) found in the inner Oslo Fjord (Norway) an almost complete advective replacement of the deep waters during the winter. The influxes continued for about two months and were correlated with the wind field.

These studies illustrate the importance of the relative densities of the resident basin water and adjacent coastal water in determining deep water exchange. The magnitudes and frequencies of influxes to these fjords however, were mixed and the driving forces responsible

for the advection of water across the sill and into deep basins were both varied and often not well defined.

Study Area

Resurrection Bay is a fjord estuary located on the Kenai peninsula of southcentral Alaska (Fig. 2). It is approximately 30 km long, 6 to 8 km wide, and oriented in a north-south direction. An inner basin 290 m deep is separated from the outer reaches of the fjord by a sill at approximately 185 m depth located south of Caines Head. The outer fjord is approximately 250 m deep and opens directly onto the Gulf of Alaska. The continental shelf area in the north-western Gulf of Alaska varies between about 50 km and 110 km in width and shoals to about 175 m approximately 70 km offshore. The fjord is bounded on both sides by mountains of around 1000 m in height. The weather is governed principally by that over the Gulf of Alaska, but the steep mountains tend to channel winds axially within the fjord. The principal source of freshwater is the Resurrection River at the head of the fjord. U.S.G.S. records show that most runoff occurs between July and September and varies between about 500 m^3 sec^{-1} and 75 m^3 sec^{-1}; the average being about 110 m^3 sec^{-1}. During the winter, freshwater input drops to below 50 m^3 sec^{-1}, and may be as low as about 10 m^3 sec^{-1}, between January and March.

Hydrographic Measurements

Five stations (Fig. 2) have been occupied since November 1972 on

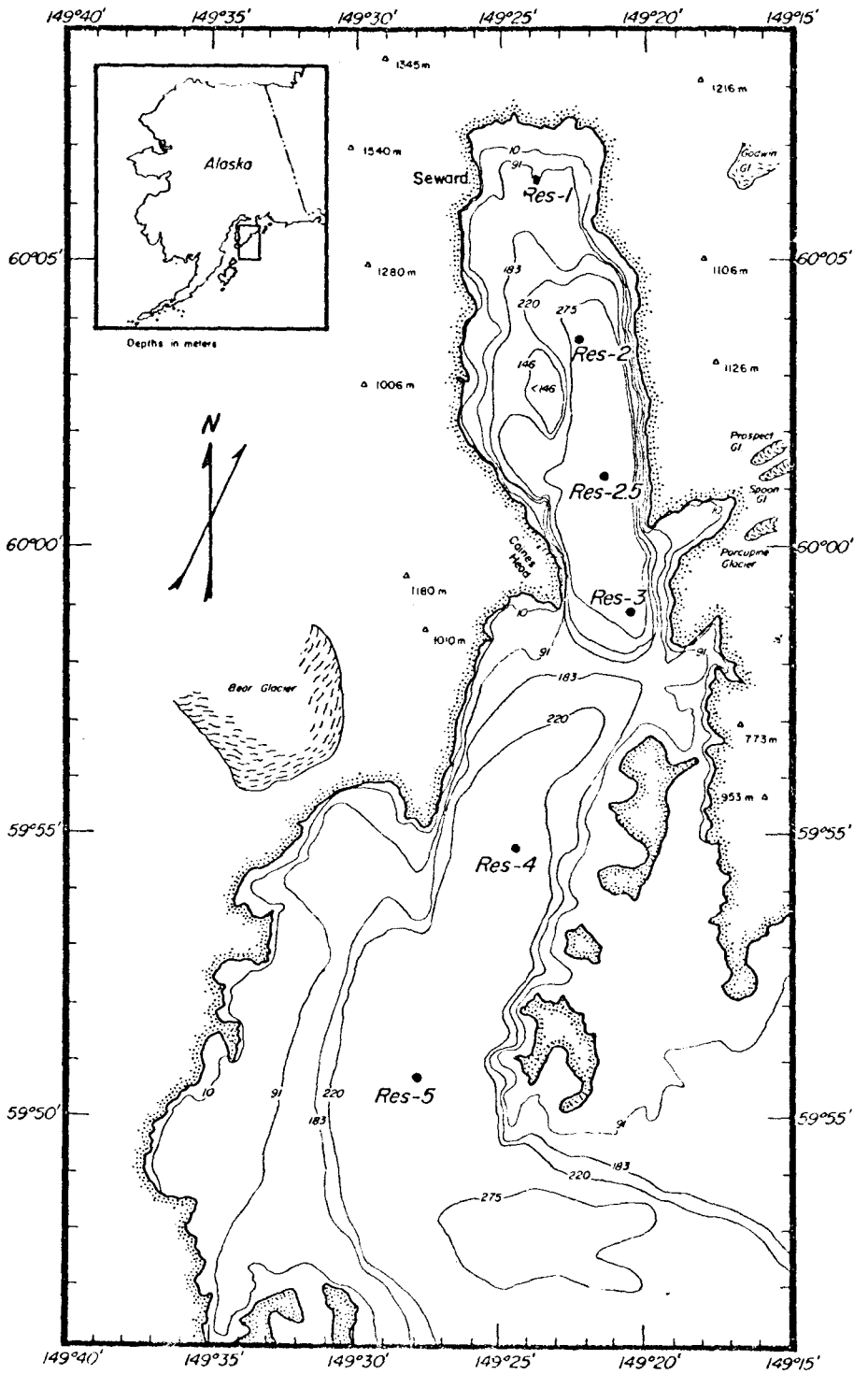


Figure 2. Map of Resurrection Bay showing station locations and depth contours.

an approximately monthly basis to obtain temperature (T), salinity (S) and oxygen (O_2) measurements. Some of these stations were sampled in less detail after initial results showed that the fjord exhibited two distinct hydrographic regimes. Two stations were selected to represent these: Res-4 for the outer fjord reaches, and Res-2.5 for the inner basin. Most of the discussion in this dissertation, refers to these latter two stations. Nansen bottles and a Bissett Berman 9040 S.T.D. (salinity, temperature, depth) were used to collect the hydrographic data. As the deep water exchange was of principal interest, discrete Nansen bottle sampling was conducted below 150 m at approximately 20-m intervals to the basin floor (290 m). The STD data obtained were calibrated using Nansen T and S data. These sample depths were selected by visual inspection of the STD chart trace, where temperature and salinity gradients were minimal (to minimize depth error effects). Differences between the discrete Nansen data and the STD data at that depth were computed. An average offset was determined over the entire cruise and this offset applied to all stations to produce a final STD printout. The accuracy and precision of the final data are considered to be ± 0.02°C and ± 0.02°/$_{oo}$ in temperature and salinity respectively. Samples for dissolved oxygen content were analyzed by the Carpenter modification of the Winkler titration.

Aanderra recording current meters were installed at Res-2.5, at depths of 42, 93, 185, and 286 m, during the oceanographic winter and spring months of March through May, and again during the late summer, September through October.

A pre-requisite to an understanding of the hydrography of Resurrection Bay is a knowledge of the seasonal variations of the water masses on the adjacent continental shelf.

Seasonal Variations in Marine Source Water: Gulf of Alaska

Royer (1975), in a two year (1970 to 1972) study of the northwestern continental shelf waters of the Gulf of Alaska, found that the seasonal variations were governed primarily by the predominating atmospheric conditions. During the winter months (October through April) the Aleutian low dominated and the associated strong easterly winds in the northern Gulf resulted in onshore (north) Ekman transport and accumulation of surface water along the coast. The resulting coastal convergence depressed the deep waters off the shelf (downwelling) and low salinity 32.00°/$_{oo}$ to 32.5°/$_{oo}$ cold, 2.0 to 3.0°C water persisted there during the winter. The North Pacific high dominated in the summer and associated with this were weak and variable westerly winds in the northern Gulf. A weak offshore (south) component of Ekman transport, (essentially a relaxation of the intense winter downwelling) permitted more dense (σ_t>26.00), saline (S >33.00°/$_{oo}$) and warmer (T $\sim$5.0°C) water which had been depressed off the shelf during the winter to be advected up onto the shelf. Further work by Royer (personal communication) has shown a similar seasonal variation in the water masses on the shelf during the years 1973 to 1976. The deep waters (>150 m) were characterized in summer by salinities >33°/$_{oo}$ and temperatures of approximately 5.0°C but, in winter by lower salinities, 32.00 to 32.50°/$_{oo}$ and cooler temperatures, approximately 3.0 to 4.0°C.

RESULTS

Variations in Salinity, Temperature and Oxygen

At the low temperatures encountered in Alaskan waters density differences are controlled primarily by salinity differences and these are therefore treated here simultaneously. The following data are intended to demonstrate the seasonal and inter-basin differences and similarities in the water structure of Resurrection Bay. The deep waters of all of the fjord are dominated by the advection of dense water up onto the adjacent continental shelf in the summer. However, in the winter the deep water behind the sill of the inner basin is relatively isolated from the flushing of the outer reaches of the fjord that occurs as a result of the downwelling at the coastline. Variations within the deep water (>150 m) are emphasized. The major hydrographic features are listed below.

Surface Waters

1. The water column was most stratified in salinity and temperature between April and November which coincided with spring and summer warming, snow melt and freshwater runoff. The stratification was intensified between August and October because of increased runoff due to rainfall. Surface salinities generally varied between 23°/$_{oo}$ and 29°/$_{oo}$, during the summer months, but were found as low as 16°/$_{oo}$ and 26°/$_{oo}$ (September 1973), in the inner and outer reaches of the fjord respectively. Surface temperatures were as high as 14°C, throughout the fjord during July months.

2. Maximum surface water salinities of approximately 31.5°/$_{oo}$, and minimum temperatures, <3.0°C, were found throughout the fjord during March and April, and resulted respectively from decreased freshwater runoff and surface heat loss to the cold, dry winter air masses. Because of thermohaline convection and other energy sources for mixing such as winds and tides, the water column exhibited minimum stability about this time.

Deep Waters

1. Maximum salinities were found throughout the entire fjord deep waters during September and October (Figs. 3 and 4). Salinities >33.00 °/$_{oo}$ (σ_t >26.00), temperatures of ∿5.0°C, and oxygen concentrations of around 4.0 ml ℓ^{-1}, were measured below about 150 m.
2. Minimum salinities were found in deep waters between March and May. There was however, a significant difference between the minimum salinities observed in the inner and outer fjord (c.f. Figs. 3 and 4). For example, at 250 m, at the outer station (Res-4) in 1975 the minimum salinity was 32.21°/$_{oo}$ (σ_t = 25.56) in February, but at the inner station (Res-2.5) at the same depth and time, the salinity was 32.79°/$_{oo}$ (σ_t = 25.88). Similar minimum salinity (density) differences for these two stations were found in the previous two years. The warping of the isopleths (Appendix A Figs. 1, 2) between the inner and outer reaches of the fjord, as a result of longitudinal temperature and salinity differences, reflects the different oceanographic conditions at the two stations.

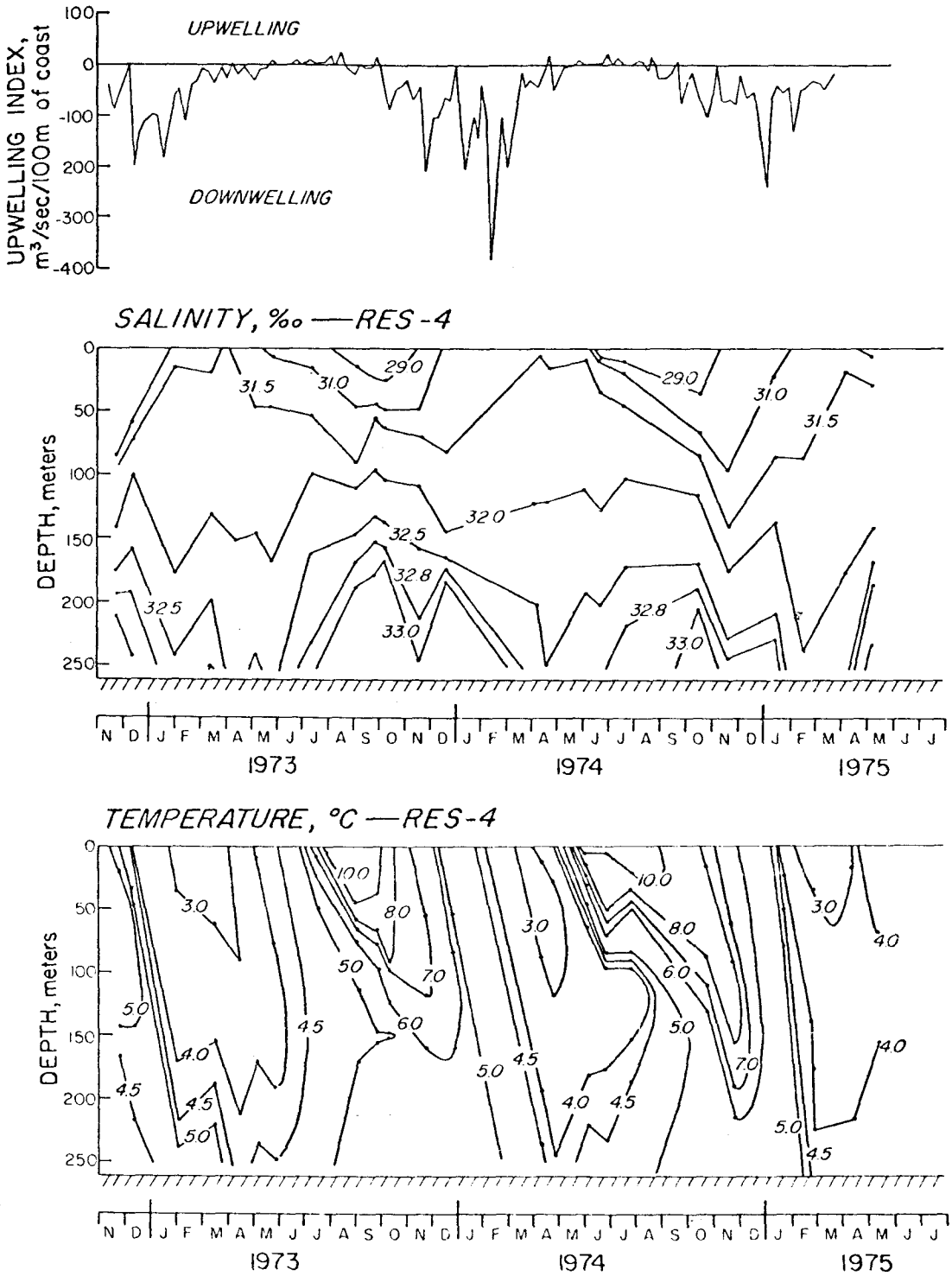


Figure 3. Seasonal variations of salinity and temperature at Res-4 (59°54.7'N, 149°24.5'W) and the upwelling index at the coastline (60°N, 149°W).

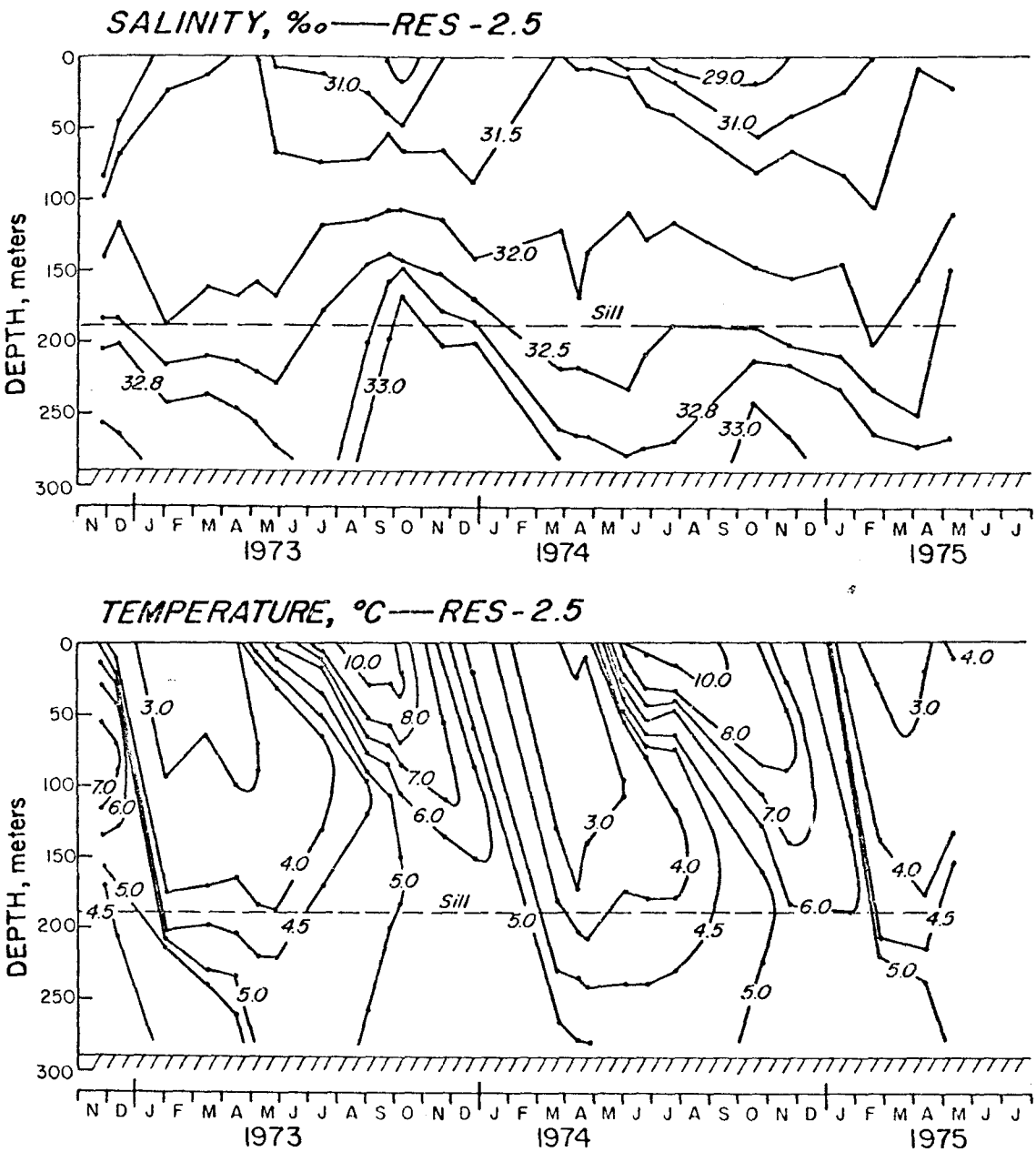


Figure 4. Seasonal variations of salinity and temperature at Res-2.5 in the inner basin of the fjord.

3. A deep pycnocline persisted at the inner station during the fall and winter months (October to April) between about 180 and 220 m (Fig. 5). This was not however, a persistent feature at the outer station (Fig. 6). During March-April the outer station exhibited minimum stability with differences in temperature and salinity from 100 m to 250 m of around 1.0°C and 0.75°/$_{oo}$ ($\sigma_t \sim 0.40$). However, at the inner station differences of this order persisted over only about a 60 m depth interval encompassing the sill (185 m). The disparities reflect the more stratified nature of the deep waters around the sill at the inner station.
4. Erratic vertical excursions of around 10 to 50 m/month were observed in isohaline and isothermal lines, below about 150 m, at the outer station Res-4 (Fig. 3). At the inner station Res-2.5, however, the vertical excursions of the isohaline and isothermal lines were only about 10 to 20 m/month (Fig. 4) and varied almost uniformly with time between October and May. The contrast between the two stations was most marked below about 150 m. At 250 m depth the overall seasonal ranges in salinities and temperatures were about 1.3°/$_{oo}$ ($33.3 > S > 32.0$), and 2.0°C ($6.00 > T > 4.0$) at Res-4, while at Res-2.5 they were less and about 0.4°/$_{oo}$ ($33.2 > S > 32.6$) and 1.1°C ($5.7 > T > 4.6$).
5. The seasonal ranges and vertical structures in oxygen contents, below about 150 m, were markedly different between the two stations Res-4 and Res-2.5 (Figs. 5 and 6). Oxygen concentrations at Res-4, varied between 3.5 and 7.5 ml ℓ^{-1} and, while concentrations generally

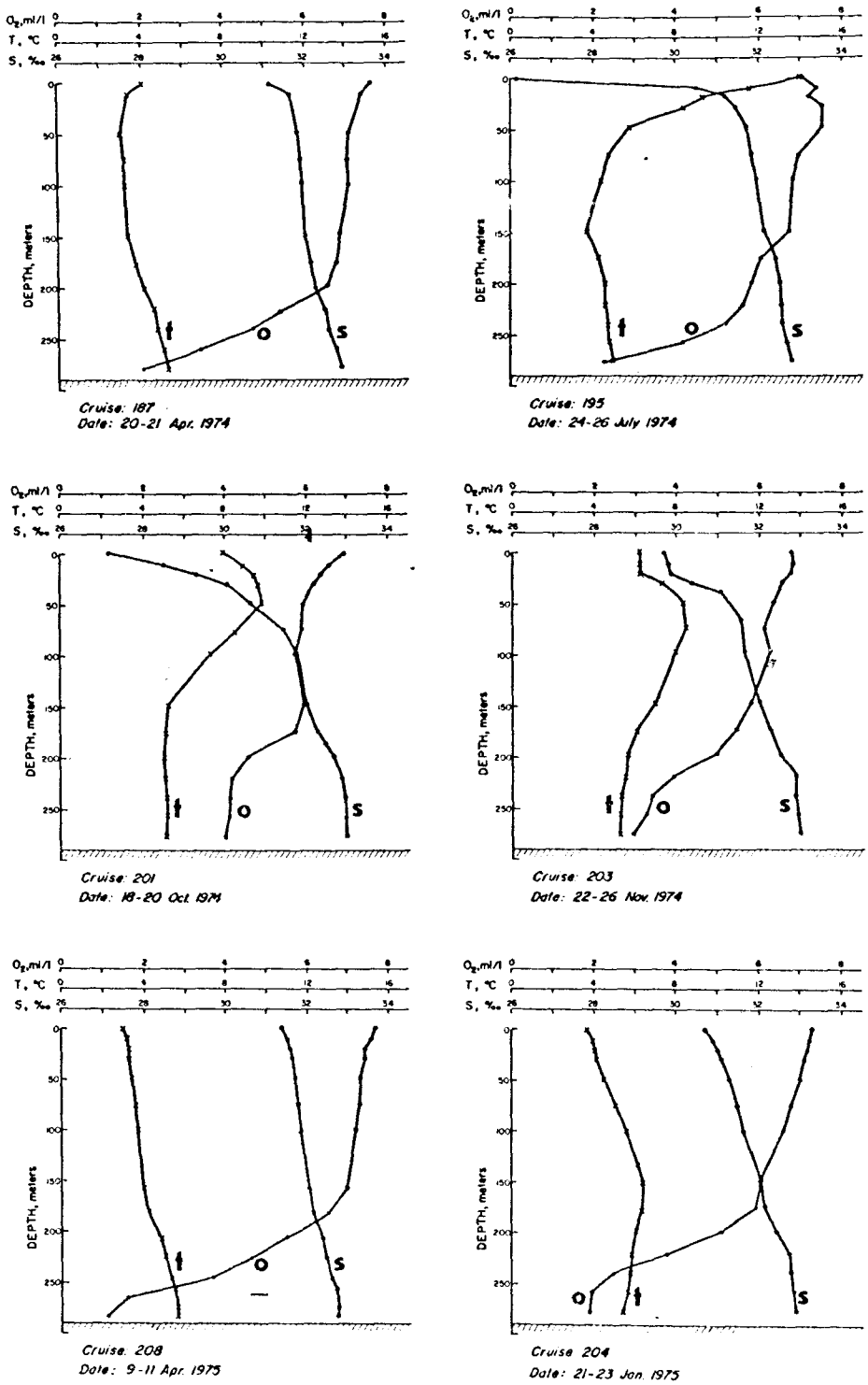


Figure 5. Vertical profiles of temperature (t), salinity (s), and oxygen (o), station Res-2.5 between April 1974 and April 1975.

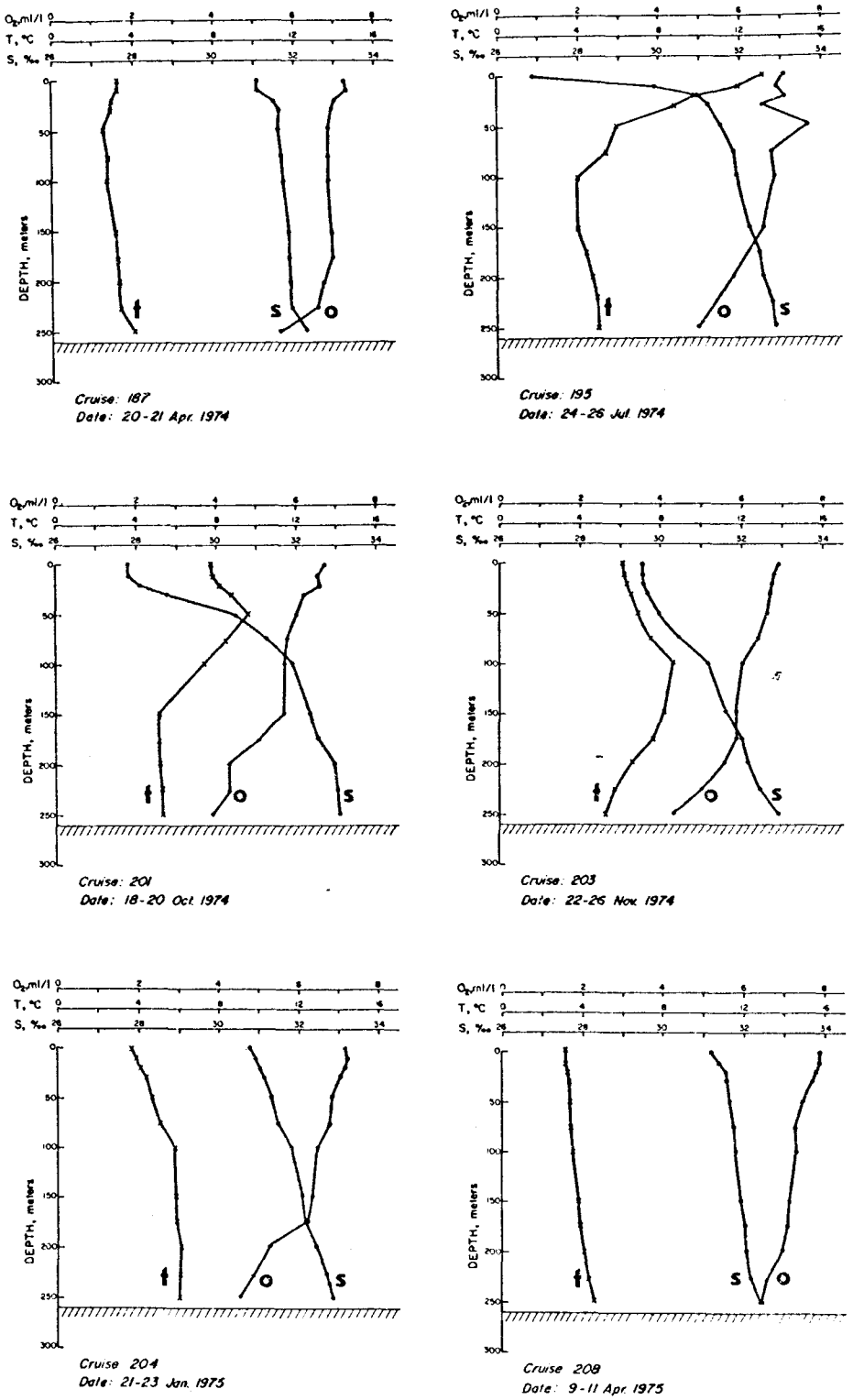


Figure 6. Vertical profiles of temperature (t), salinity (s), and oxygen (o), station Res-4 between April 1974 and April 1975.

decreased with depth, both maxima and minima were found throughout the water column. The seasonal variations at depth were erratic, similar to the temperature and salinity variations (noted previously). At Res-2.5 concentrations varied between about 1.0 ml ℓ^{-1} and 7.5 ml ℓ^{-1} and always decreased with depth. Concentrations at the sill depth (185 m) generally increased throughout the winter months to about 7.0 ml ℓ^{-1}, but toward the bottom (290 m) decreased to about 1.0 ml ℓ^{-1}. An oxygen gradient, directed into the deep basin developed and intensified between October and April (Fig. 5).

Current Meter Observations

These data are considered only briefly here to complement the hydrographic observations. The directions and average speeds are shown in Table 5. The winter records indicate a net inflow between 93 and 185 m and the persistence of northerly (down estuary) winds during these months probably resulted in a net outflow at the surface. At 185 m an average speed of 1.13 cm sec^{-1} at 35° (inward) was computed, but at 286 m a 'drift' 0.25 cm sec^{-1} was computed at 147° (outward). The latter record did not show any features of the record at the sill depth (185 m), but appeared dominated by semi-diurnal tidal fluctuations only. During the time period of this record, there was a net loss of salt out of the basin and a consequent decrease in density.

The summer records indicate a circulation pattern very different from that of the winter. At 285 m an almost continuous inflow (north) was recorded with an average speed of 3.1 cm sec^{-1} and net outflow was

TABLE 5

Current Meter Data

Z (meters)	March 13-May 8 1973 Average Speed cm sec^{-1}	Direction degrees	September 5-October 9 1973 Average Speed cm sec^{-1}	Direction degrees
42	Meter	Flooded	3.69	8 (I)
93	0.77	11 (I)*	0.88	119 (0)
185	1.13	35 (I)	1.13	179 (0)
286	0.25	147 (0)#	3.11	28 (I)

* (I) inflow

(0) outflow

measured at the sill (185 m) and at 93 m. While the current meters were in place successive increases in salinity (hence density) in the basin were observed on three observation periods (Fig. 4).

DISCUSSION

Summer Conditions

Inner and Outer Fjord

Time series representations of salinity in the outer basin and weekly means of the coastal upwelling indices, computed for a 3° grid centered about 60°N 149°W, located off the entrance to Resurrection Bay in the Gulf of Alaska, are shown in Fig. 3. The indices were computed from distributions of the surface atmospheric pressure (Bakun, 1973). A negative index indicates onshore transport (coastal convergence and downwelling) and a positive value offshore transport (coastal divergence and upwelling).

The general features of this plot are similar to Royer's (1975) data and show the divergence of the isohaline surfaces during the winter months (October through April), with decreasing salinities in deep water, and the convergence of the isohaline surfaces during the summer when maximum salinities were found below 150 m. The appearance of more dense (σ_t >26.00) water on the continental shelf during the summer resulted from a relaxation of the coastal convergence and the downwelling conditions (Royer 1975). The relatively dense water (σ_t > 26.00, S > 33.00°/$_{oo}$ and T $\sim$ 5°C) was evident throughout the outer and inner reaches of Resurrection Bay during September and October

(Figs. 3 and 4). The successive density increases observed together with inflow at 286 m (Table 5), in the inner basin, can be explained by the advection of more dense water across the sill which sinks to the basin floor and displaces the less dense resident basin water upward. The outflow (south) between 185 m and 92 m probably represents the displaced water. It is proposed, the flow into the deep basin, is controlled by the horizontal density gradient across the sill. The current meter records (Heggie, 1977) indicate that flow into the basin appears to be impeded when winds within the fjord are northerly; a reflection of longshore east winds in the Gulf of Alaska, and coastal convergent conditions. These latter cause isopycnal surfaces in the outer reaches of the fjord to be depressed and the horizontal density gradient across the sill is decreased.

Winter Conditions

Outer Fjord

The winter data indicate that different processes control the temperature and salinity distributions of the inner and outer regions of the fjord. Royer (1975) assessed the importance of convection with vertical mixing as a control on the water structure on the shelf and found that mixing to 250 m *via* this mechanism was improbable. Although vertical isopycnal conditions were not observed at the outer station (Res-4) the water column was least stable between February and April. Convective cooling with vertical mixing would result in an increase in density; but this latter was not observed in the deep water >150 m during

the winter months. Convective cooling with vertical mixing is limited to the upper 100 m in Resurrection Bay and the general depression of the isohaline (Fig. 3) and therefore the isopycnal surfaces below about 100 m between October and April, must result from the downwelling of less dense surface water. The more dense (σ_t > 26.00, S > 33.00°/$_{oo}$, T $\sim$ 5.0°C) water present in the outer reaches of the fjord during October has been swept down and out of the fjord by the downwelling of surface water. The densities at 250 m ($\sigma_t \sim$ 25.5) at this station (Res-4) between February and April were similar to those on the adjacent continental shelf.

The erratic vertical excursions in the salinity and temperature isopleths observed in the outer reaches of the fjord (Res-4) below 150 m during the winter months can be explained by advective processes. Although the sampling frequencies of the two data sets are different, a comparison of the salinity (density) and upwelling index variations (Fig. 3) suggests that depressions in isohaline surfaces are preceeded by or coincide with downwelling (coastal convergence) conditions. Conversly, elevations in isohaline surfaces follow or coincide with relaxations of downwelling conditions. The erratic vertical excursions of the isopleths appear to reflect the relative intensities of the coastal convergences. The accumulation of water at the coastline drives the dense bottom water out of the fjord, and conversly, relaxations of the coastal convergence permit more dense water to flow into the fjord from the adjacent gulf.

Inner Fjord

At the inner station (Res-2.5), both the temperature and salinity time-series plots below about 150 m are generally different from those observed at the outer station discussed above. The only similarities are in the variations of the 32.00°/$_{oo}$ isohaline surface which fluctuates between about 100 and 200 m. This implies that, between these depths, the same processes control the time distributions of salinity and density at these stations. The water masses advected through the outer fjord from the Gulf of Alaska penetrate the inner fjord across and above the sill (185 m). However, the more uniform decrease in salinities in the inner fjord basin (Fig. 4), indicates that water below the sill is generally not subject to advective influxes. Although the probability of influxes into the inner basin is low during the oceanographic winter and spring months (because of less dense water on the adjacent shelf) occasional influxes have been observed. However, at these times only some fraction of the basin water behind the sill was exchanged. This is in contrast to the complete advective replacement that takes place during September and October. Influxes were observed during early winter (December, 1972, 1973) when remnants of the summer upwelled water might have still existed on the adjacent shelf, and during spring (March 1973, April 1974, April and May 1975) when the density of the resident basin water approached an annual minimum and relatively more dense water appeared in the outer fjord (Fig. 4).

The changes in temperature and salinity below the sill varied in a quasi-uniform fashion during the winter (October through April). The

temperature distributions reflected warming of the deep water due to the vertical exchange of heat from the temperature maximum created during the summer. Temperatures around the sill depth ranged between about 5.0 and 6.0°C by January. The rapid erosion of the warm water core throughout the winter by surface heat loss resulted in a decrease of the temperature around the sill to 3.5 to 4.5°C by mid-March. Temperatures at 280 m varied over a more narrow range $\sim$ 0.5°C compared to an $\sim$ 2.5°C range at the sill, over the approximate seven month winter period. Salinities decreased during the winter, and like the temperatures, varied at the bottom of the basin over a narrow range $\sim$ 0.35°/$_{oo}$ compared to an $\sim$ 0.70°/$_{oo}$ variation around the sill, over the same time period. The distributions of temperature and salinity in the deep waters of the inner basin during the winter (October through April; Fig. 7) resulted predominately from a vertical turbulent exchange across the sill by mixing of the more dense (S $\sim$ 33.00°/$_{oo}$ T $\sim$ 5.0°C) water that was advected into the basin during the summer with the less dense (S $\sim$ 32.00°/$_{oo}$ to 32.50°/$_{oo}$, T $\sim$ 3.0 to 5.0°C) water found on the shelf during the winter.

Advective exchange of the deep water of the inner basin appeared to begin again around May or June when the density of the resident basin water has decreased during the previous winter months by vertical mixing. Influxes were observed to penetrate to about 270 m in June and July of 1974, but amounted to only about 20% of the basin volume, although in May of 1975 approximately 90% of the basin water was replaced.

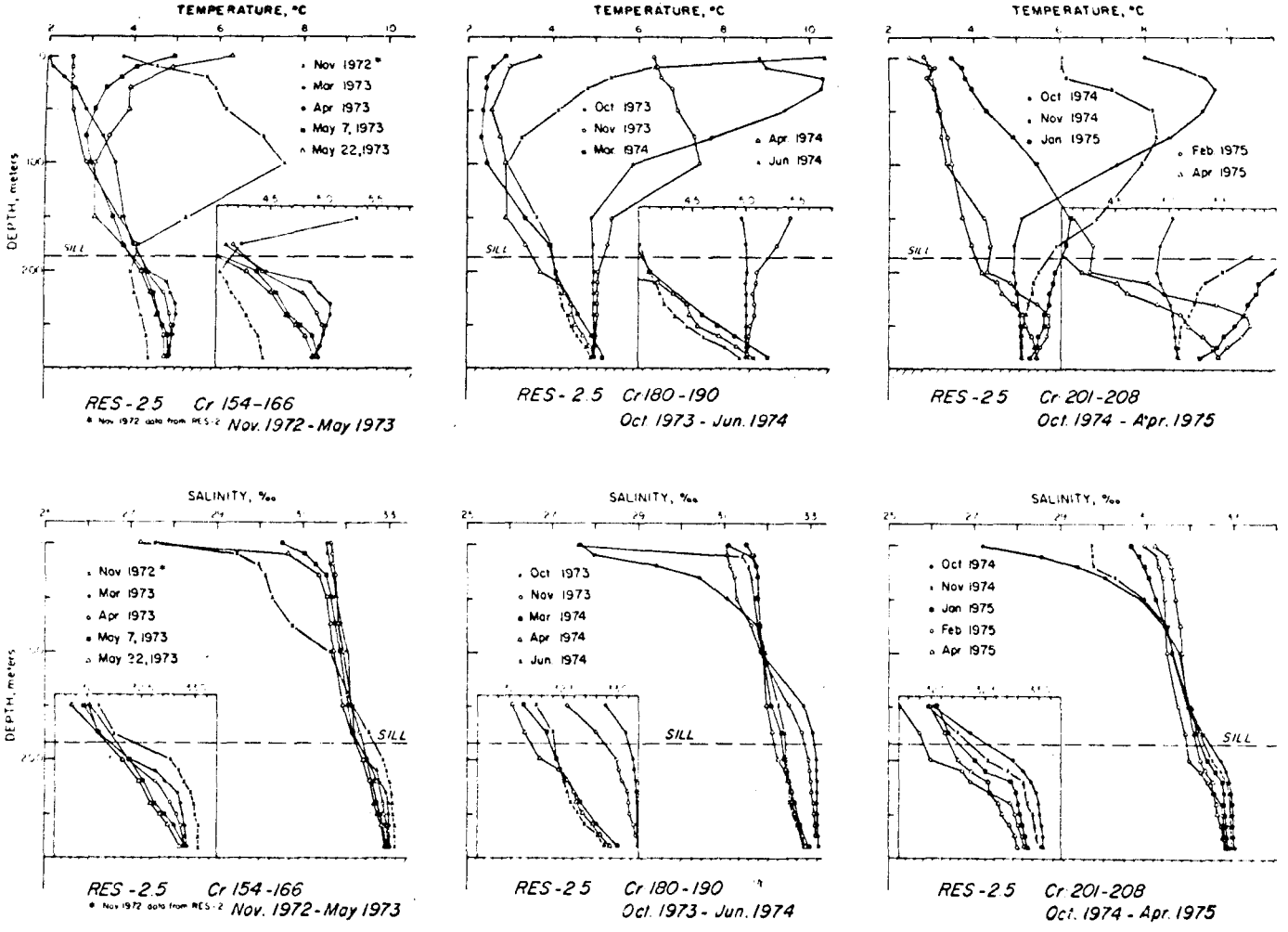


Figure 7. Vertical profiles of salinity and temperature at Res-2.5 during the winter months of 1972-73, 1973-74, and 1974-75.

The density of the marine source waters had increased sufficiently (σ_t > 26.00) by September or possibly earlier to lead to the complete renewal of the deep and bottom waters of this basin.

This cycle of advective renewal of the deep water in the summer and fall followed by vertical eddy exchange throughout the winter months has been observed in the inner basin over a period of three years. The exchange processes are examined quantitatively below.

Vertical Turbulent Exchange Across the Sill

The rates of transfer of heat and salt are characterized by coefficients of eddy conductivity and eddy diffusion respectively. For any parcel of water, the determination of mixing coefficients from budget considerations depends upon the quantitative evaluation of all export and input terms (Sverdrup *et al.*, 1942). Salinity and temperature are conservative properties, i.e., they are changed by external processes only at boundaries and in the bulk of a fluid are affected by advection and diffusion only; distributions of temperature and salinity have commonly been used to determine turbulent mixing coefficients.

Rattray (1967) found, using similarity methods, that the rate of change of salinity in the deep water of fjords was a balance between horizontal advection and vertical diffusion. The contribution to the salt and heat budgets, in the deep water below the sill, from horizontal advection has been difficult to evaluate in Resurrection Bay. The stations in the inner basin reflected reasonable homogeneity in temperature and salinity, although occasional analytically significant differences

have been observed (Heggie *et al.*, 1977). There was no evidence of consistent longitudinal gradients in temperature or salinity and, in the absence of these, the horizontal advection term in the budget equation becomes insignificant. There was however, certainly some motion in this basin as evidenced by the varying slopes in the salinity (density) profiles below the sill, e.g., October 1974. The latter period however, was one of (or shortly after) extensive advective renewal of the deep water and it might be expected that dense water once advected into the basin would undergo some oscillatory motion until damped by friction. Mean flow at and above the sill depth during the winter months, might have also induced some compensating flow below the sill. However the persistence of a vertical pycnocline through the sill depth region would tend to dampen any induced flow, and part of the energy associated with horizontal flow, above the sill, would be redistributed into energy for vertical turbulent mixing across the pycnocline. Horizontal motion in the basin (excluding direct influxes of dense water across the sill), can be convective in nature, resulting from longitudinal temperature and salinity differences or, be of a seiche type generated by intermittent surges in horizontal flow above the sill.

The distributions of salinity and temperature during the winter months have been expressed as one-dimension diffusion equations. Lateral and longitudinal advection and diffusion terms and vertical advection have been omitted. The simplified salt balance equation used here is therefore:

$$\frac{\delta \bar{S}}{\delta t} = - \frac{\delta}{\delta Z} \left(K_z \frac{\delta \bar{S}}{\delta Z} \right) \qquad (2.1)$$

where Z is depth, $\frac{\delta S}{\delta t}$ is the time change of salinity, K_z is the vertical mixing coefficient and $\frac{\delta S}{\delta Z}$ is the vertical salinity gradient. The heat budget equation is similar but S (salinity) is replaced by the product of Cp (specific heat) and T (temperature). The rate of loss of salt from a parcel of water bounded by the sill depth and the basin floor (ρ is density) is given by (assuming no salt flux across the basin floor):

$$-\int_{\text{bottom}}^{\text{sill}} \frac{\delta(\rho\bar{S})}{\delta t} \cdot dZ = K_z \frac{\delta(\rho\bar{S})}{\delta Z} \text{ (sill)} \qquad (2.2)$$

i.e., the rate of salt loss is the product of the vertical diffusion coefficient at the sill and the average gradient of salinity across the sill between the time periods of the observations (Appendix A). The expression states nothing about the distribution of K_z between the sill and the basin floor. Equations of this type have been used to compute coefficients $K_z(s)$ and $K_z(t)$ at the sill depth (Table 6). Some further aspects of the salt and heat budget equations are discussed in Appendix A. The most significant computational error is the subjectiveness associated with determining vertical salinity and temperature gradients across the sill. As it was difficult to define exactly where the transition between the advective and diffusive regimes occurred, the gradients have generally been determined over about a 40 m depth interval (180 to 220 m) encompassing the actual sill depth (185 m), and are subject to about a 20% error.

TABLE 6

Coefficients of Eddy Diffusion and Conductivity at 200m, Res-2.5

Cruise and Date		$K_Z(s)$ $cm^2\ sec^{-1}$	$K_Z(t)$ $cm^2\ sec^{-1}$
146	November 21, 1972		
148	December 9, 1972	1.2	9.2*
154	February 3, 1973	3.1	-11.1**
160	March 14, 1973	2.5	2.2
161	April 3, 1973	2.2	2.9
163	May 7, 1973	4.5	3.1
166	May 22, 1973		
180	October 9, 1973	6.7	6.1
182	November 17, 1973		
183	December 17, 1973	7.3	-29.9**
186	March 27, 1974	4.2	6.3
186#	April 15, 1974		
187	April 21, 1974	1.9	2.5
190	June 10, 1974		
201	October 18, 1974	2.1	7.2
203	November 26, 1974	1.6	6.4
204	January 21, 1975	4.4	-24.6**
206	February 27, 1975		

* Significant longitudinal temperature differences suggest a contribution from horizontal advection.

** Gradients in the temperature distributions change sign which introduces large uncertainties into the time average.

Single lines indicate partial advective replacement of deep basin water.

Double lines indicate complete advective replacement of deep basin water.

The calculated coefficients (Table 6) are within the general range of vertical eddy mixing coefficients determined by Craig (1969) of 0.1 to 10 $cm^2\ sec^{-1}$. They are consistent with coefficients determined in similar deep-silled basins, e.g., Sholkovitz and Gieskes (1971), of 4 to 6 $cm^2\ sec^{-1}$, but are higher than those determined in basins where vertical diffusional exchange is suppressed by a pycnocline. Spencer and Brewer (1971), found $K_Z = 0.14\ cm^2\ sec^{-1}$, in the main halocline of the Black Sea, and Fanning and Pilson (1972) determined a minimum $K_Z = 0.06\ cm^2\ sec^{-1}$, in the upper 700 m of the Cariaco Trench. The agreement between the coefficients determined from both salt and heat is good considering the assumptions involved in the computations.

Vertical Advective Exchange Across the Sill

It was noted earlier that occasionally during the winter months the density of the water in the basin behind the sill increased. This observation can be explained by the advective input of water, located beyond the sill, with a density greater than the density of the resident basin water. Advected horizontally across the sill the dense water can sink a level of equal density inside the basin. This section examines the volumes of water involved, and the vertical advective velocities associated with this type of exchange.

Advective exchanges of this type, during the winter are intermittent only in character. Often, between two time periods when the density of the basin water had increased there was no evidence of

water at the outer station (Res-4), around the sill depth of a density high enough to penetrate into the basin (e.g., CR:160, March, 1973; CR:192, June, 1974; CR:208, April, 1975). This means that the dense water had, at some time between the two measurement periods, been advected across the sill to penetrate into the basin and had then been rapidly removed out of the fjord. Such reasoning is consistent with the erratic and rapid changes in the isohaline and isothermal surfaces and density changes at Res-4 discussed earlier.

The following computations utilize data from Res-2.5 and are believed to be representative of the inner basin. Two approaches have been adopted which differ only in the form of the advection term. Equations may be written for the salt budget which state that the observed salt change between any two time periods is a contribution from an increase by advection across the sill, and a loss across the sill by diffusion. Each of the terms in the following expressions are explained in detail and examples of the computations given in Appendix A.

The advective contribution in the first approach is expressed as a product of the difference between the average salinities of the influxed (S_I) and the effluxed (S_E) basin water, and a transport (volume/time). For a unit horizontal cross-sectional area the budget equation is:

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta S}{\delta t}\, dZ = (\bar{S}_I - \bar{S}_E)\, \frac{1}{\Delta t} \int_{o}^{h} dZ - K_z \int_{\text{bottom}}^{\text{sill}} \frac{\delta^2 S}{\delta Z^2}\, dZ \qquad (2.3)$$

The time change and diffusive terms and both S_I and S_E were evaluated

from the observed salinity distributions. Solution of the equation yields a volume of water influxed into the basin and an average vertical velocity.

The second approach expresses the advection term as a product of a vertical velocity W_Z and a salinity gradient, $\frac{\delta S}{\delta Z}$.

$$\int_{Z^*}^{\text{sill}} \frac{\delta S}{\delta t}\, dZ = W_z \int_{Z^*}^{\text{sill}} \frac{\delta S}{\delta Z}\, dZ - K_z \int_{Z^*}^{\text{sill}} \frac{\delta^2 S}{\delta Z^2}\, dZ. \qquad (2.4)$$

*Z is the depth to which the influx penetrated, identified as the depth at which there was no density change between the two time periods. The equation was solved first for W_Z, and the volume of water influxed into the basin was W_Z x Δt x horizontal cross-sectional area.

Some assumptions and boundary conditions common to both approaches are listed below.

1. The influx, for the convenience of calculations only, continues for the total time period between observations. This assumption however does not represent a realistic physical situation; the consequences are discussed later.
2. W_Z and K_Z are constant between the sill depth and depth of penetration of the influx over the time period of the influx.
3. Horizontal and lateral advection and diffusion terms are small compared to the vertical terms.
4. There is no salt or heat exchange across the basin floor.

The volumes of water and the vertical velocities associated with the advective exchanges are listed in Tables 7 and 8.

TABLE 7

Percent Volumes of Water Displaced During an Advective Influx to The Inner Basin Computed From Salt and Heat Budgets

Cruise and Date		Method 1		Method 2	
		Salt	Heat	Salt	Heat
154	February 3, 1973	50%	74%	40%	50%
160	March 14, 1973				
166	May 22, 1973	60%	62%	82%	82%
171	July 6, 1973				
182	November 17, 1973	†__	45%	50%	__*
183	December 17, 1973				
187	April 21, 1973	22%	17%	30%	33%
190	June 10, 1974	17%	18%	12%	14%
192	June 28, 1974	20%	22%	15%	32%
195	July 25, 1974				
206	February 27, 1975	41%	34%	27%	29%
208	April 9, 1975	95%	83%	-ξ	-ξ
210	May 13, 1975				

Computations break down as ΔT sill/Z → limit of precision of measurements.

†Computations break down as $(\overline{S}_I - \overline{S}_E)$ → limit of precision of measurements.

ξComputations break down as ΔT sill/Z* and ΔS sill/Z* → limit of precision of measurements.

Single lines indicate extensive summer renewal of the deep water.

TABLE 8

Vertical Advection Velocities Associated with Influxes to the Deep Basin

	Method 1.				Method 2.			
	Salt Budget		Heat Budget		Salt Budget		Heat Budget	
CRUISE	cm s^{-1} ($\times 10^{-3}$)	m yr^{-1}	cm s^{-1} ($\times 10^{-3}$)	m yr^{-1}	cm s^{-1} ($\times 10^{-3}$)	m yr^{-1}	cm s^{-1} ($\times 10^{-3}$)	m yr^{-1}
154 160	1.5	477	2.2	703	1.2	380	1.5	464
166 171	1.5	491	1.6	491	2.1	657	2.1	657
182 183	---		1.8	599	1.9	599	---	
187	0.5	158	0.4	119	0.7	233	0.8	241
190	1.1	333	1.1	333	0.8	234	0.9	281
192 195	0.8	254	0.9	292	0.6	190	1.3	420
206	1.2	377	0.9	272	0.8	234	0.8	234
208 210	2.6	806	3.0	947	---		---	

The September-October current meter records documented the influx of more dense water across the sill and penetration to the basin floor with displacement of the resident basin water upward and out of the inner fjord between about 190 and 100 m depth (Table 5). These data were used to compute the volume and the vertical velocity of the water advected through the basin during the advective exchange of 1973. The average vertical cross-sectional area of the inner basin between the sill depth and basin floor is about 2.9×10^5 m^2, and combined with a net north (inward) speed of 1.62×10^{-2} m sec^{-1} results in a transport of about 5×10^3 m^3 sec^{-1} which, in 35 days (length of current meter record), is equivalent to a volume of about 1.5×10^{10} m^3; sufficient to replace the topographic basin volume ($\sim 3.5 \times 10^9$ m^3) about four to five times over. If it is assumed that the transport (5×10^3 m^3 sec^{-1}) falls vertically through a horizontal cross-sectional area encompassed by the sill depth contour ($\sim 5 \times 10^7$ m^2), the vertical velocity is about 1×10^{-2} cm sec^{-1} or approximately 3000 m yr^{-1}.

A comparison of this vertical velocity with those listed in Table 8 indicates it to be about an order of magnitude higher. It should be remembered however, that the velocities listed in the table were computed assuming the influx took place over the total time period between observations and this is unrealistic. Data show that influxes were not continuous. The time period over which each influx occurred was impossible to determine precisely, but it probably depended upon the relative intensity of the driving force responsible for elevating the more dense water above the sill and maintaining it there such that

inflow into the basin could occur. Some clues to the time scale of these sporadic influxes however were obtained from the March to May current meter record at the sill (185 m), which showed horizontal excursions across the sill into the inner basin, that persisted for one to three days (Heggie, 1977). Assuming that when more dense water appeared at the sill, it was advected into the basin over similar time periods, the velocities reported in Table 8, would be increased about one order of magnitude. Velocities adjusted this way agree reasonably well with those computed directly from the September through October current meter records.

Non-Conservative Distributions: Oxygen Consumption

Organic carbon either produced *in situ* in surface waters by photosynthesis or introduced as terrestrial runoff in coastal waters becomes a source of food for heterotrophic organisms. The degradation of carbon requires oxygen, which is obtained most favorably from dissolved molecular oxygen as long as it is available in the water column (Mechalas, 1974). If the organic carbon supply rate is greater than the rate of supply of molecular oxygen, the activities of the heterotrophs may rapidly reduce the oxygen levels, and anoxic conditions may result. The latter is rarely found in the water column, except in deep basins of restricted circulation e.g., Cariaco Trench, Black Sea, and Lake Nitinat, but often develops in near surface sediments. Oxygen consumption rates are important in controlling the flux of carbon through the hydrosphere. The following analyses present average oxygen

consumption rates in the water column of the inner basin of this Alaskan fjord.

Figure 5 shows that immediately after the advective replacement of the basin water in September and October, the oxygen levels were around 4.0 ml ℓ^{-1}. Throughout the following winter months oxygen levels at the sill increased to about 7.0 ml ℓ^{-1}, but deep in the basin (280 m) they decreased to about 1.0 ml ℓ^{-1} by March or April; a gradient directed into the basin developed and intensified between October and April. It should be noted that the quantity of oxygen in the basin during September and October was approximately equal to that in the basin during March and April. However, the marked changes in the vertical distribution with time reflect contributions from input and export processes. It is proposed that these distributions are a balance between input across the sill by vertical eddy mixing and losses due to biological consumption in the basin. The following equation (O_2 is dissolved oxygen concentration and R is the biological oxygen consumption rate below sill depth) expresses this:

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta O_2}{\delta t}\, dZ = -\int_{\text{bottom}}^{\text{sill}} \frac{\delta}{\delta Z}\left(K_Z \frac{\delta O_2}{\delta Z}\right) dZ + \int_{\text{bottom}}^{\text{sill}} R\, dZ \qquad (2.5)$$

If the diffusive input is greater than the time change term, R is negative and represents a net consumption. The general depth distributions of oxygen at the three stations in this basin were all similar. Some longitudinal differences however were observed which may be the

result of spatial differences in consumption rates related to sources of supply of organic carbon.

Oxygen budgets have also been considered during the time periods when advective replacements of water across the sill have occurred. The budget can be written in the following equation form, again assuming no longitudinal or lateral contributions:

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta O_2}{\delta t}\, dZ = \{\bar{O}_{2(I)} - \bar{O}_{2(E)}\} \frac{1}{\Delta t} \int_{o}^{h} dZ \; - K_Z \int_{\text{bottom}}^{\text{sill}} \frac{\delta}{\delta Z} \left(\frac{\delta O_2}{\delta Z}\right) dZ + \int_{\text{bottom}}^{\text{sill}} R \times dZ \qquad (2.6)$$

The advective contribution to the oxygen budget has been computed by comparing the oxygen concentration of the water advected into $(O_{2(I)})$ the basin with the average oxygen concentration of water effluxed $(O_{2(E)})$ from the basin. The details of each of the above types of computations are given in Appendix A. Average water column oxygen consumption rates are listed in Table 9. The consumption rates determined, during advective exchange, are marked with an asterisk in the following table. These data are consistent with average consumption rates determined from other fjords; Barnes and Collias (1958), for example, found rates varying between 1.8 and 7.3 ml ℓ^{-1} yr^{-1} (mean, 5.8 ml ℓ^{-1} yr^{-1}) in fjords of Puget Sound. The rates determined in this study varied between 1.1 and 7.6 ml ℓ^{-1} yr^{-1} (mean, 3.7 ml ℓ^{-1} yr^{-1}).

SUMMARY

Deep water exchange between the Gulf of Alaska and Resurrection Bay, schematically shown in Figure 8, occurs principally during the

TABLE 9

Average Water Column Oxygen Consumption Rates Below the Sill at Resurrection Bay Station 2.5

Cruise	and Date		Consumption Rate Integrated (R·dZ) ml cm^{-2} yr^{-1}	Consumption Rate Average (R) ml ℓ^{-1} yr^{-1}
160	March	14, 1973	15.3	1.5
161	April	3, 1973	16.9	1.7
163	May	7, 1973	11.0	1.1
166	May	22, 1973		
180	October	9, 1973	14.7	1.5
182 *	November	17, 1973	41.6	4.2
183	December	17, 1973	39.3	3.9
186	March	27, 1974	55.0	5.5
186	April	15, 1974		
187	April	21, 1974	22.8	2.3
190 *	June	10, 1974	52.0	5.2
192 *	June	28, 1974	26.0	2.6
195	July	25, 1974		
201	October	18, 1974	68.7	6.9
203	November	26, 1974	69.0	6.9
204	January	21, 1975	17.6	1.8
206 *	February	27, 1975	76.0	7.6
208 *	April	9, 1975	28.2	2.8
210	May	13, 1975		

*Advective contribution to the oxygen budget accounted for (see equation 2.6).

oceanographic summer months (June through October), and is a direct result of the advection of more dense water up onto the continental shelf. The relatively dense water ($\sigma_t > 26$) is advected horizontally into the inner fjord basin and, *via* gravitational displacement, sinks to replace the resident water of the deep inner basin. Over a 35 day period during September and October 1973, the transport through the basin was determined to be sufficient to replace the topographic basin volume four to five times over. The rapid change in atmospheric conditions, and hence the wind field over the Gulf of Alaska between about September and November depresses isopycnal surfaces at the coastline and drives the more dense summer water mass down and out of the outer reaches of Resurrection Bay. The water that penetrates below the sill during the summer remains isolated for the following winter period and exchanges with the less dense winter water masses above the sill predominately *via* vertical eddy mixing. Advective exchange across the sill begins again around May or June of the following year and is complete by October. The sequence of advective exchange in the summer and diffusive exchange in the winter has been observed in the inner fjord basin for three years (1972-1975). The advection of dense water into the basin during oceanographic summer probably occurs annually and is effected by a decrease in density of the basin water during the preceeding winter and the appearance of more dense water at the sill due to the seasonal change in the water masses in the adjacent Gulf of Alaska.

Salt and heat budgets were utilized to examine characteristics of the exchange processes. Eddy mixing coefficients between 1.2 and 7.2 $cm^2\ sec^{-1}$ were found during the winter months. Vertical advective velocities of the order of 10^{-3} to 10^{-2} cm sec^{-1} were found associated with influxes to the deep basin. Data of these types were employed to examine non-conservative behavior of oxygen and to compute rates of oxygen consumption in the deep water. Consumption rates were found to vary between 1.1 and 7.6 ml $\ell^{-1}\ yr^{-1}$, and were in the range of consumption rates determined from some other fjord environments. A knowledge of the deep water exchange processes in the fjord forms the framework to examine non-conservative behavior and to compute fluxes of chemical elements. The utility of the inner basin of Resurrection Bay as a 'geochemical bucket' is justified on this basis and in the following chapters the non-conservative behavior of copper is examined.

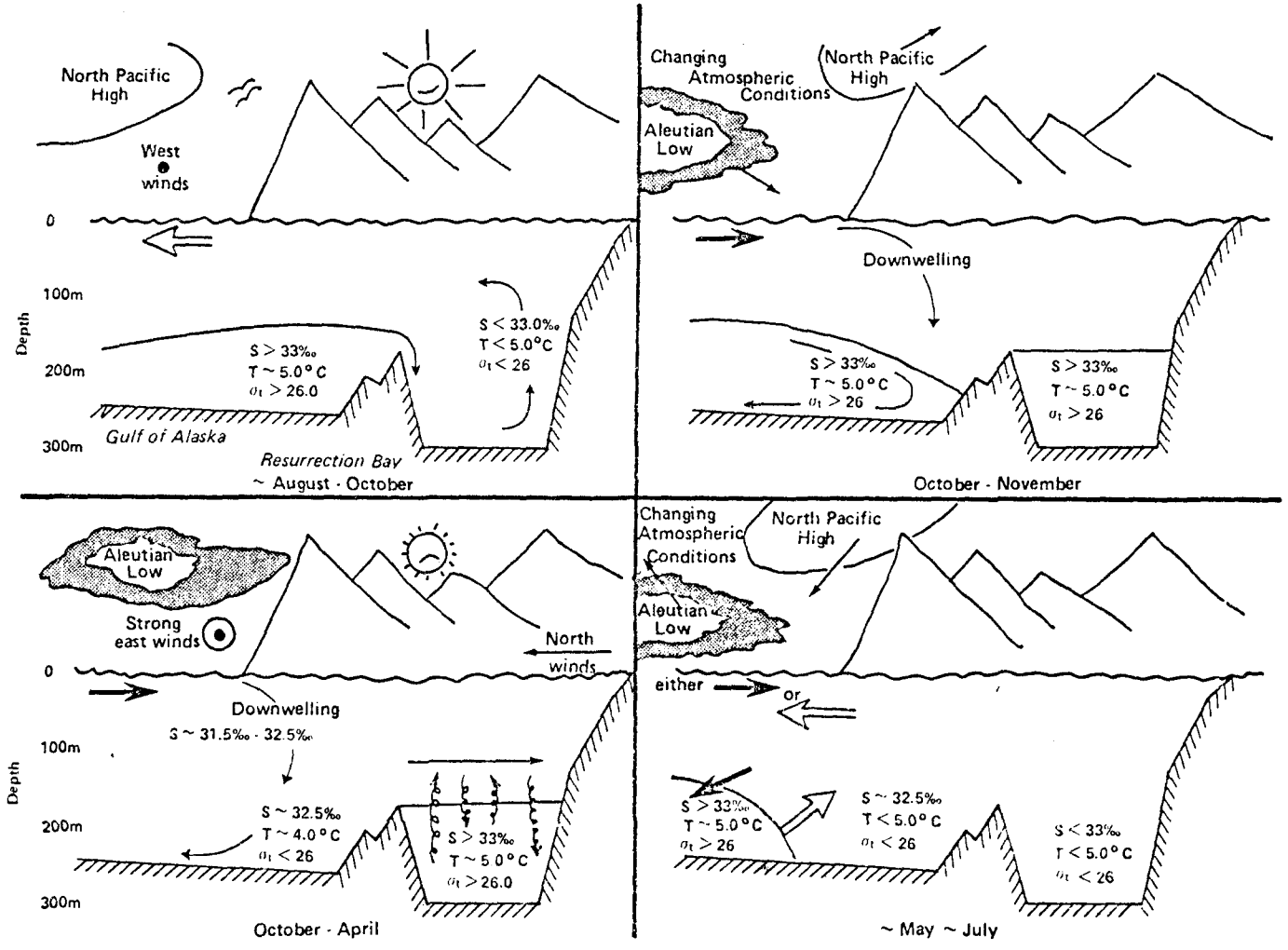


Figure 8. Schematic representation of the seasonal exchanges of water between Resurrection Bay and the Gulf of Alaska.

III. DIFFERENTIAL PULSED ANODIC STRIPPING VOLTAMMETRY: MEASUREMENTS OF COPPER IN SEAWATER

Because the 'trace' metallic elements in the oceans exist at such low concentration levels ($\sim 10^{-9}$ mole ℓ^{-1}) there are only a few methods that are sensitive enough to detect and quantitate these elements. Atomic absorption spectrometry has been used to determine a large number of elements in natural waters (Burrell, 1975) but in seawater a pre-concentration step, either through cation exchange resins (e.g. Riley and Taylor, 1968) or by solvent extraction techniques (e.g. Brooks *et al.*, 1967) is required. The chemical pre-treatment procedure detracts from these methods as the possibility of contamination increases with the number of handling steps. Neutron activation is specific for several elements but concentration and chemical separation steps are required for many of the trace metals including copper (Robertson and Carpenter, 1976). Neutron activation methods are not in widespread use because of the specialized nuclear treatment and handling equipment necessary. Anodic stripping voltammetry (an electrochemical technique) is applicable only to the determination of a few of the common trace elements in seawater (e.g., Cu, Pb, Cd, Zn). However, the particular advantage that it offers for specific element studies over the above techniques is that it is not subject to contamination *via* concentration and separation techniques; the element of interest in seawater may be directly determined.

The method, in general, involves reduction of metal ions from an electrolyte (seawater), into a 'working' electrode, at a potential more

negative (cathodic) than the reduction potential of the metal of interest. The 'working' electrode may be either a hanging mercury drop (HMDE) or thin mercury film coated onto a carbon electrode (TFE). After concentration of the metal of interest into the working electrode, the metal is oxidized from the electrode, by scanning a suitable potential range in an anodic direction:

$$Me \gtrless Me^{n+} + ne$$

The resultant current has both a capacitative contribution due to charging of the electrical double layer around the electrode-solution interface and a faradaic component due to oxidation of the metal atom. Resolution of the latter is desired as it is related to the concentration of metal in solution:

$$i = n\ FDA\ \frac{C.}{\delta.}$$

where: i = faradaic current

n = number of electrons involved in the oxidation

D = diffusion coefficient

F = faraday number

A = electrode area

δ = diffusion layer thickness

C = bulk solution concentration

Although the necessary equipment is relatively simple, electrochemical methods in general have not seen widespread use in natural, and in particular seawater analyses, because;

i. at the very low concentrations encountered the faradaic current is not easily resolved from the capacitative current, and

ii. electrode stability and lifetimes have proved to be frustrating problems.

Electrochemical Methods in Natural Water Analyses: Historical

The hanging mercury drop electrode (HMDE) was sufficiently sensitive to detect trace metallic elements in seawater but prohibitively long plate times were required for quantitative analysis. The sensitivity could be improved by using faster scan rates, but at the HMDE the faradaic component of current is proportional to the square root of the scan rate, but the capacitative current is directly proportional to scan rate (Kemula and Kublik, 1963) hence, the background current increases more rapidly than the desired faradaic component.

Thin film electrodes (TFE), made by electroplating mercury onto a solid inert substrate such as carbon, permitted greater sensitivities to be obtained than could be had with the HMDE, and improved the peak resolution. As the faradaic current at a TFE is directly proportional to the scan rate (Roe and Toni, 1965) much faster scan rates could be used. The surface-volume ratio in the TFE is also much greater than that at the HMDE and hence the concentration of metal in the electrode for any given plating time is greater and significantly shorter analysis times could be used. In seawater the most common TFE has been the MCGE (mercury coated graphite electrode). The electrode described by Matson *et al.*, (1965) was made by coating a graphite rod with paraffin; one end being polished and plated with a mercury film. Electrodes treated this way however require frequent polishing and often have short lifetimes. Glassy carbon was described as a promising electrode

material (Zittell and Miller, 1965) but application to the analysis of several elements in various sample types was first described by Florence (1970) and in seawater and marine samples by Florence (1972).

At the n.mole ℓ^{-1} level long plating times and high background currents have prevented linear d.c. scanning methods being adopted as convenient and routine analytical tools. Several approaches have been used including; a.c. polarography (Underkofler & Shain, 1965) and pulsed voltammetry (Parry and Osteryoung, 1965; Christian, 1969) to descriminate against the background (capacitative) current and Zirino and Healy (1972) applied a differential linear d.c. anodic stripping method to seawater analysis. There appeared recently several papers which have described the technique of, and applications of the differential pulsed mode of ASV (Flato 1972; Siegerman and O'Dom, 1972; Osteryoung and Osteryoung 1972; Christie *et al.*, 1973; Copeland *et al.*, 1973a; Copeland *et al.*, 1973b) on new commercially available instrumentation.

One objective of the work reported here was to combine the glassy carbon electrode with the differential pulsed mode of ASV, to investigate if this union could overcome some of the common problems: short useful electrode lifetimes, poor peak resolution, long plating times because of poor sensitivity, and poor analytical reproducibility, that have hindered the use of electrochemical methods in marine trace metal geochemistry.

Electrodes and Things

A Coleman Instruments calomel electrode 3-712 was used as the reference electrode and a counter electrode was made by inserting a piece of platinum wire into the end of a hollow glass tube. Electrical contact was made *via* a mercury pool and a tungsten wire. A Sargent-Welch pH combination electrode (S-30070-10), to monitor sample pH, was inserted into the electrolysis cell. It was necessary to replace the electrolyte in commercial electrodes with several times recrystalized KCl to prevent trace metal leakage into and contamination of the sample. Working electrodes were prepared by sealing, with epoxy resin, a piece of glassy carbon (grade GC-A, Tokai Carbon Co., Ltd.), 6 mm dia. x $\sim$ 6 mm in a glass tube. The electrode surface was levelled with fine grade emery cloth and polished with various grades of Buchler powdered alumina. An electrode made this way could be used for several months without repolishing. Electrical contact between the glassy carbon working electrode and the PAR 174 was made *via* a mercury pool and a tungsten wire. A rotating working (glassy carbon) electrode, because of stirring action, increases mass transport to the electrode during electrolysis therefore permitting greater sensitivities than could be obtained in unstirred solutions. A small hollow chuck and belt drive system was constructed and mounted to a small bodine motor (Talboy Engineering Co.). The hollow chuck fitted with two silicone 'O' rings, facilitated the exchange of electrodes and provided a rigid mounting that minimized electrode 'wobble'. The cell used in this work was conical shaped and designed to handle 10 to 25 ml volumes of sample

and to facilitate sample transfer such that a large number of samples could be analysed with a minimum of handling and exposure.

Optimization of Experimental Conditions

The effect of mercury concentration in determining film thickness and peak currents of the species of interest on glassy carbon electrodes has been investigated previously (Florence, 1970; Erickson, 1973), and was not repeated in this work. Electrodes were usually plated for about 10 to 15 minutes at -0.1V from either filtered acidified (pH $\sim$ 2.5) seawater, or 0.6 M KCl, solutions which were $\sim 4 \times 10^{-5}$ M in mercury.

It was noted very early in this work that metal peak currents, peak resolution and peak oxidation potentials in the differential pulsed mode were functions of scan rate, modulation amplitude and other parameters. The optimum conditions for quantitative analysis were evaluated by holding several machine parameters constant and varying a different parameter through the given instrument range. The optimum conditions are summarized in Table 10, details are given in Appendix B. The method of standard additions was used for quantitation of copper concentrations, necessitating a linear response to additions of a known standard over the concentration range of interest. With the conditions stated previously such a linear response to copper additions was obtained (Fig. 9a), and copper could be determined quantitatively in seawater by differential pulsed ASV, using a rotating electrode with

TABLE 10

Optimum Conditions for Analysis of Copper in Filtered and Acidified (pH ∿ 2.5) Seawater Samples.

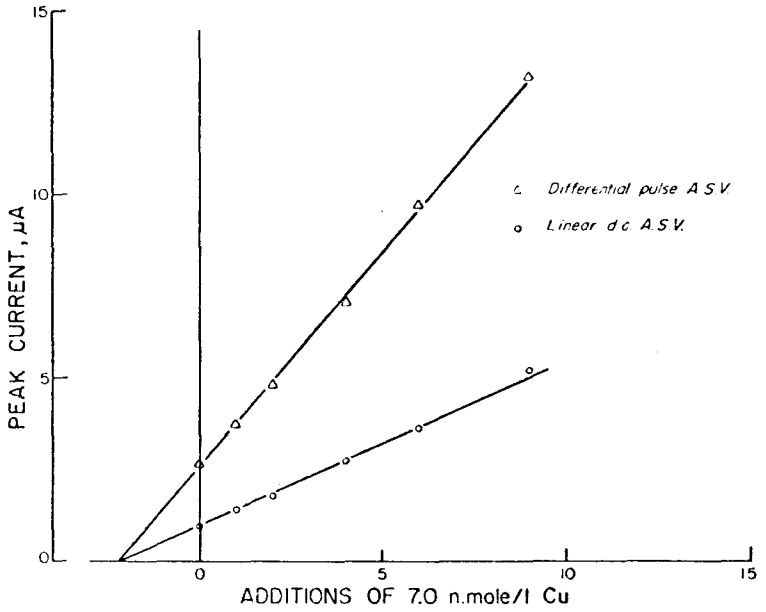
Electrode plated 5 to 15 min at -0.1V, from seawater solution ∿ 4×10^{-5} M in Hg^{++}

Scan rate:	5 mV sec^{-1}
Modulation amplitude:	50 mV
Plate potential:	-0.75V
Pulse repetition:	0.5 sec
Plate time:	3 to 10 mins depending upon sample concentration
Electrode rotation:	∿ 1500 rpm

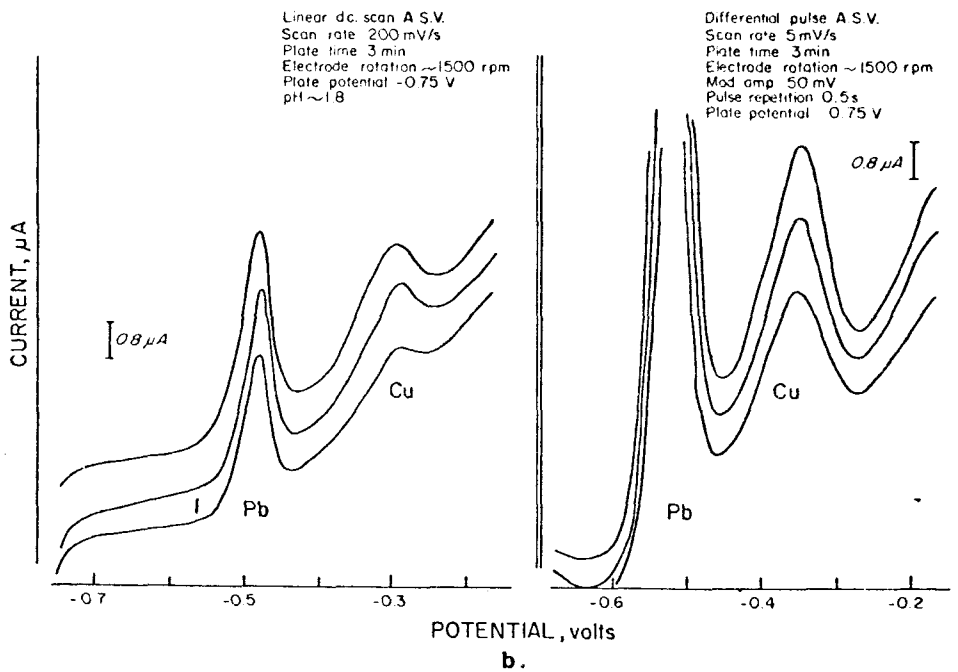
about a fivefold increase in sensitivity over linear d.c. scan ASV (Fig. 9b).

Analysis Procedure

1. A sample of seawater was pipetted into the electrolysis cell, the electrode was rotated and nitrogen gas bubbled through the sample for about 10 to 15 minutes.
2. A 'test' plate-strip cycle (to determine optimum plate time for any sample) was completed by plating the electrode for about 5 minutes (-0.75V): 15 seconds prior to the termination of the plate step the nitrogen gas flow and electrode were stopped and the electrode was scanned (5mV sec^{-1}) from -0.75V to about -0.15V; copper and lead peak heights were recorded. Two further plate-strip cycles were completed and the copper peak current recorded in duplicate.
3. The electrode was held at about -0.15V, for about 1 to 2 minutes while a standard addition was added to the sample and mixing in the solution completed.
4. The plate-strip cycle was repeated and the increase in copper peak height computed. At least two standard additions were made to every sample.
5. A plot of peak height vs copper concentration was constructed; the concentration in the sample was found by graphical extrapolation. The complete analysis of a single sample took about 50 minutes.



a.



b.

Figure 9. Comparisons of linear d.c. and differential pulsed ASV:
a. standard additions plot
b. current-voltage relationships.

Precision of Analyses

The average concentration of copper in seawater, reported in the recent literature, is about 8 n.moles ℓ^{-1} (0.5 µg ℓ^{-1}; Brewer, 1975). This work was designed to compare copper concentrations in Resurrection Bay in space and time. Although sensitive measurements could be made with the differential pulsed technique it was necessary to maintain a high degree of precision, at the low metal concentrations encountered in seawater, to effectively examine for non-conservative behavior. As a measure, mostly, of the confidence in the procedure adopted for sample collection and treatment, the same Niskin bottle was lowered to the same depth (280 m) over about a 14-hr period in the 'isolated' deep inner basin of Resurrection Bay. This approach also served to provide some measure of the variability associated with sampling through time (assumed sampling to the same water mass). The reproducibilities (coefficient of variation) associated with the procedure through sampling and analysis are shown in Table 11.

The main source of error in the laboratory analysis of a single sample was the reproducibility associated with standard additions of copper to the electrolysis cell. Beckman microliter pipettes were used and 5 and 10 µℓ additions of 8.7×10^{-6} M copper were added. A 10 µℓ addition was equivalent to a copper concentration in the cell of 3.5×10^{-9} M. Standard solutions were prepared, from a 8.7×10^{-2} M stock solution, each time a batch of samples were to be run. The Beckman microliter pipettes were chosen principally because the solution is stored in a reservoir, attached to the dispenser, and remains free from

TABLE 11

Analyses of Precision of Copper Determinations by Differential Pulsed A.S.V.

INDIVIDUAL MEASUREMENT		WITHIN NISKIN BOTTLE		BETWEEN NISKIN BOTTLE	
Samples from 250 ml aged seawater pH∿2.2		Samples drawn from the same Niskin bottle		Single sample drawn from the same Niskin bottle cast to 280m, over a 14 hr period	
Sample	Cu n.moles ℓ^{-1}	Sample	Cu n.moles ℓ^{-1}	Sample	Cu n.moles ℓ^{-1}
1	9.60	S_1	4.25	A_4	9.61
2	8.98	S_2	3.78	B_4	11.81
3	8.82	S_3	4.41	C_4	11.02
4	9.45	S_4	4.25	D_4	10.08
5	9.76	S_5	3.78	F_4	12.13
6	9.13	-	-	N_{16}	11.65
	$\bar{x}$ = 9.29		$\bar{x}$ = 4.09		$\bar{x}$ = 11.02
	σ = 0.38		σ = 0.30		σ = 1.00
% Coefficient of variation = 4.0%		% Coefficient of variation = 7.3%		% Coefficient of variation = 9.2%	

atmospheric contamination during continued extended use. This was considered more desirable than exposing a standard solution to the atmosphere each time an addition to the cell had to be made, as is the case when Eppendorf type pipettes were used, and dipping of pipette tips into the standard was also considered undesirable. The Beckman microliter pipettes, however, had one disadvantage: dispensers proved difficult to keep clean and after some use small beads of solution adhered to the microliter dispenser walls resulting in inaccurate volume additions. This problem required constant attention and frequent cleaning of the dispensers were necessary, it is probably the main source of error in individual laboratory analyses. All things considered the overall precision (coefficient of variation) for these analyses is about ± 10%.

Interferences

The determination of copper in natural waters by anodic stripping voltammetry is potentially subject to interferences from other metals which form intermetallic compounds with copper in the mercury film and from surface active agents that accumulate on the electrode surface.

At plate potentials more negative than about -1.0V both nickel and zinc form intermetallic compounds with copper. If quantitative analyses of copper only are desired, the interference from zinc and nickel can be eliminated by plating at a potential where the latter are not electroactive. All copper determinations hence were carried out at -0.75V. Seitz (1970), however, pointed out that silver interferes

with copper determinations by forming a Ag-Cu intermetallic that is presumably not stripped from the electrode during the oxidation step, but because of the large differences in concentrations of copper and silver in seawater the effect is likely to be small, and to produce somewhat low determinations for copper. The extent of any silver interference in copper determinations in seawater was briefly examined in this work. Samples of seawater containing approximately 15 n.mole Cu ℓ^{-1} (pH $\sim$ 1.5) were taken and the peak height recorded in duplicate and again after successive additions of approximately 10^{-5} M Ag solutions. At a final silver ion concentration of $\sim 5 \times 10^{-8}$ M about a 25% decrease in the copper peak height was found (Fig. 10a). The concentration of silver was about two orders of magnitude greater than that believed to be in seawater ($\sim 4 \times 10^{-10}$ M; Brewer, 1975), therefore any silver interference would be less than 1%. Copper peaks from natural seawater samples remained constant after the first plate-strip cycle. Copper peaks were recorded on the second and third plate-strip cycles using a calomel, rather than a Ag/AgCl, reference electrode, and the glassy carbon electrode was replated (to prevent accumulation of any Ag-Cu intermetallic) with a thin mercury film each day prior to analyses.

The adsorption of surface active compounds onto the electrode surface may cause deterioration of the electrode and loss of sensitivity or may interfere directly, *via* chemical reaction, with analysis (Reilley and Stumm, 1962). Myers and Osteryoung (1974) pointed out that in 0.1 M KNO_3 solution at pH 4.2 Triton -X 100 (.0001%) produced a

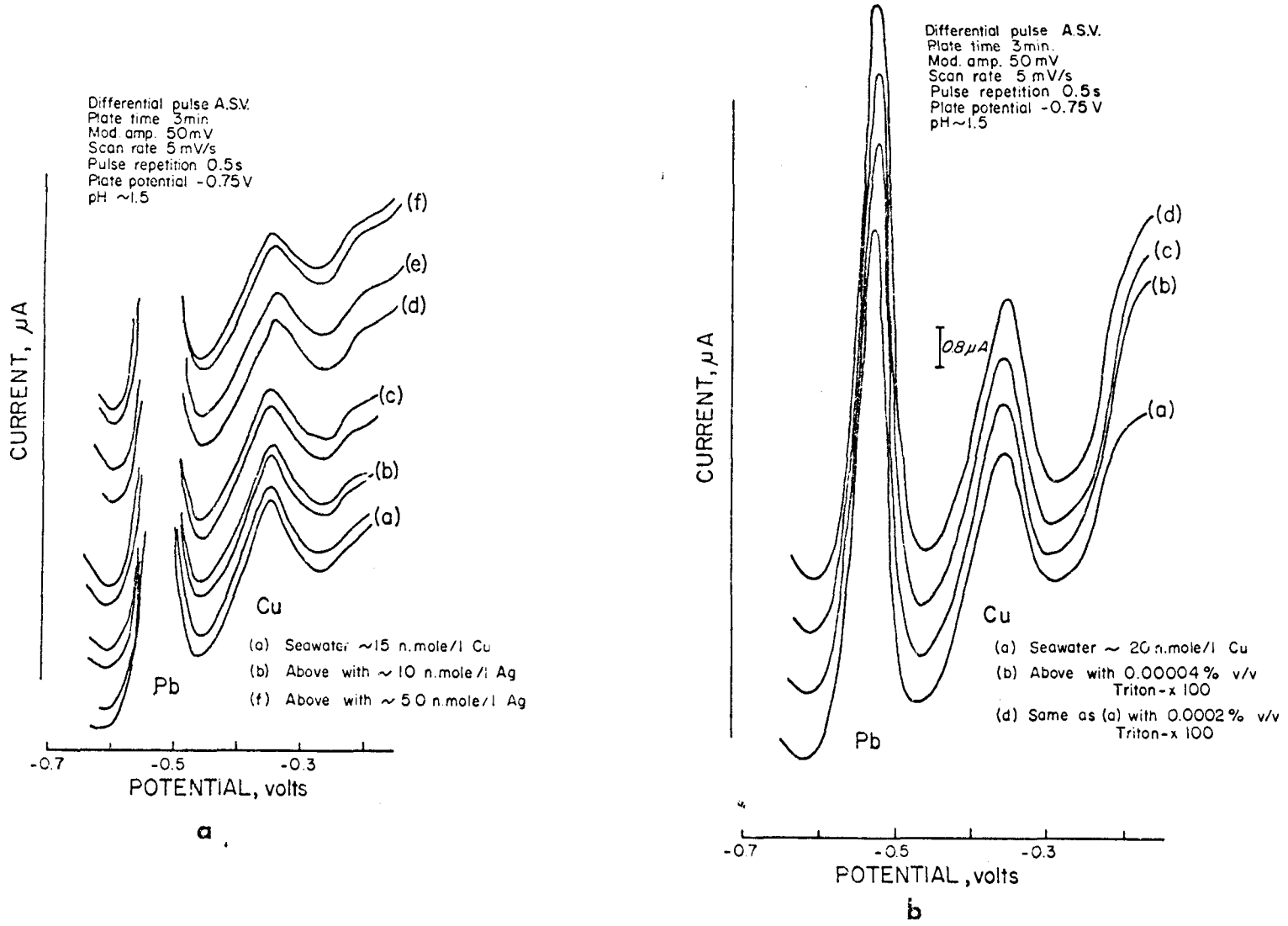


Figure 10. Effect on copper peak currents of additions of: a. $\sim 10^{-8}$ M silver; b. triton -x 100.

differential pulsed peak at about the same potential as copper and interferred with analyses. However, in this work successive additions of Triton -X, 100 up to about 0.0002% v/v, to a seawater solution (pH ∿1.5) containing about 15 n.mole ℓ^{-1} of copper indicated (Fig. 10b) no effects on the faradaic or background capacitative currents. Successive peak height increases would have been expected, but none were observed, had an interference of the type described by Myers and Osteryoung (1974) been present. Cadmium and lead peak currents however were interferred with in several samples; the cause was not found, but the effects are described in Appendix B.

Interstitial water samples however indicated some interference in copper determinations. An apparent peak, large, broad but indistinct, appeared over the region between about -0.1 and -0.40V, making direct copper determinations impossible even in acidified (pH ∿ 1.8) samples (Fig. 11b). These samples were subjected to ultra violet oxidation (∿ 3 hours) in small volume (25 ml capacity) quartz cells after the addition of about 0.1 ml of 5N nitric acid. The broad peak disappeared, after irradiation, from all samples and copper determinations were possible. The interference was observed in all interstitial water samples except those from the surface segments (0∿7 cm) of cores. The copper peak in surface samples was not masked, and direct measurements could be made without subjecting the samples to U.V. oxidation (Fig. 11a). For continuity reasons all interstitial water samples were U.V. oxidized. The contrast between these voltammograms obtained from different regions of the sediment suggests that some chemical species, possibly

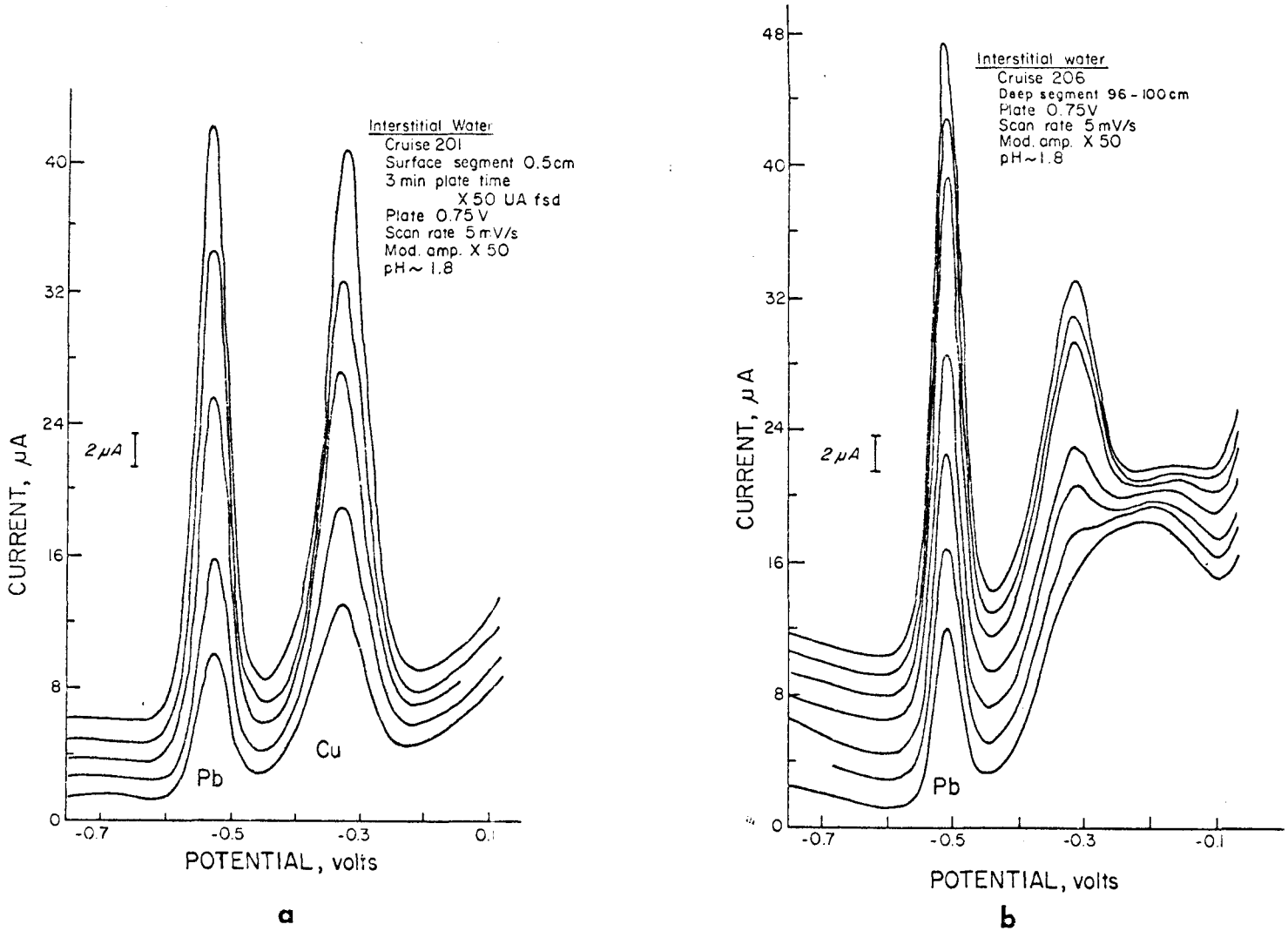


Figure 11. Representative copper and lead peak currents from and standard additions to: a. surface ~ 5 cm interstitial waters; 4.4 x 10^{-8}M Cu, 6.7 x 10^{-9}M Pb, and b. deep ~100 cm interstitial waters; 0.7 x 10^{-8}M Cu, 1.1 x 10^{-9}M Pb.

surface active agents, were present in the interstitial water samples below the sediment surface, and were electroactive under acidic conditions. High molecular weight polymeric type compounds that result from organic matter degradation and accumulate in sediments may have been responsible for the interference.

Accuracy

Trace metals appear in various forms in the sea, in solution as complex ions and associated with inorganic and organic particulate material. A common cutoff between particulate and soluble fractions is somewhat arbitrarily defined at 0.4 μm. The membrane filterable or 'soluble' fraction includes; free trace metal ions, inorganic ion pairs and complexes and organic complexes and metal ions bound to higher molecular weight materials such as lipids and humic acids (Stumm and Balinski, 1973). The operational definition of 'soluble' for trace metals is analogous to other operationally defined fractions such as 'reactive' silicate. Measurements of copper in the 'soluble' fraction have been concentrated upon in this work.

An intercalibration study of some trace metals in seawater indicated that copper determined in Pacific Deep Water and Caribbean Deep Water by a variety of methods was only poorly calibrated (Brewer and Spencer, 1970, unpublished manuscript). As the samples for intercalibration were from a single source, the variations encountered between laboratories must have been due to specificity of the different methods to different copper fractions or to contamination introduced during

processing and analysis. Only recent calibrations (Boyle and Edmond, 1975b; Bender and Gagner, 1976) have verified the reliability of different techniques. Anodic stripping methods have also been intercalibrated and recent data (Erickson, 1973) are contributing to the establishment of the reliability of these methods. Several samples in this work have been analyzed by differential pulsed A.S.V., linear d.c. A.S.V. and a neutron activation technique. At the time of writing this thesis the neutron activation data were not available; the data analyzed by the different ASV techniques are summarized in Table 12. The samples were analyzed by different operators using different sets of apparatus; agreement between the data sets is encouraging.

Two sets of samples have been analyzed in the above. One set was taken from the Gulf of Alaska to examine natural levels of copper and the other was prepared simply by mixing 'aged' seawater samples in the laboratory. The concentrations in these latter samples have no meaning with respect to natural levels but it was felt they would serve as an independent comparison of the methods. The Gulf of Alaska samples were collected in 30-ℓ drop top Niskin bottles and filtered under pressure into precleaned, 1-ℓ polyethylene containers. Two separate aliquots were collected, one for each participating laboratory. All samples were acidified to pH $\sim$ 2.0; the containers sealed in polyethylene bags and stored frozen.

TABLE 12

Comparison of Copper Concentrations in Seawater Samples Determined by Differential Pulsed ASV and Linear d.c. ASV

Sample No.	Differential pulsed ASV Cu μg ℓ^{-1}	Linear d.c. ASV† Cu μg ℓ^{-1}
L#1	0.60 0.56	0.57 0.56
L#2	0.31	0.31
L#3	0.43	0.38
L#4	1.84	1.90
EGA#24 410	0.16 0.15	0.14 0.14
EGA#15	0.21 0.15	0.14
EGA#11 1350 m	0.17	0.14
WGA#110 173 m	0.12 0.11	0.23*

† Analyst M. L. Lee

* Suggested contamination

Sample Collection and Storage

Seawater Collection

The determination of trace elements in the oceans at concentrations of about 10^{-9} M is subject to errors at several stages of any given procedure; initially during the collection of a sample from the oceans, through any sample treatments and during machine analysis. The average concentration of copper in seawater ($\sim 8 \times 10^{-9}$ M; Brewer, 1975) is about one order of magnitude lower than what the commonly accepted concentration was a decade ago ($\sim 5 \times 10^{-8}$ M; Goldberg, 1965); a consequence of improved instrument technology and an increased appreciation of handling problems associated with trace metal sample collection and storage.

The following procedure was used for sample collection and treatment:

(1) Seawater samples were collected in 1.7-ℓ Niskin bottles hung on a 3/16" GIPS (galvanized improved plow steel) wire that was used for STD work. The surface Niskin bottle was lowered about 5 to 7 m below the sea surface and returned to the surface before closing, flushing about 30 ℓ of seawater through the bottle. Niskin bottles have been known for some time to introduce zinc contamination into the sample from the surgical tubing (e.g., Robertson, 1968; Burrell, personal communication), but copper levels in the tubing are low (Robertson, 1968) and the bottles used in this work had long been equilibrated with seawater. Quality control was maintained on the bottles by noting their history of use.

(2) Samples were taken from the Niskin bottles as soon as possible after retrieval (< 1 hr) into 250 ml pre-cleaned polyethylene bottles. The sample bottles were rinsed well with three aliquots of seawater; the fourth aliquot was collected. The polyethylene bottles used were cleaned by soaking for 24 hrs in ∿ 30% v/v hydrochloric acid, rinsed a further three times with ∿ 10% hydrochloric acid and finally with de-ionized double distilled water three times.

(3) After collection the samples were filtered as soon as possible (generally < 1 hr) through Nuclepore (0.4 μm) filters (presoaked and washed with ∿ 10% hydrochloric acid, rinsed and stored in de-ionized double distilled water) which were retained in a Millipore polycarbonate filter tower. The sample was transferred totally into the filter tower, the lid replaced and approximately 15 to 20 ml filtered into the same sample container used for collection; the container was rinsed and the filtrate discarded. The polyethylene bottle was rinsed at least twice with the filtered seawater. The remaining sample except for about 10 to 15 ml was filtered under vaccuum (< 10 psi) into the storage flask; the final volume collected was about 200 ml. All equipment was handled with polyethylene gloves during filtration.

(4) The filtered samples were immediately acidified with ∿ 0.5 ml of ∿ 4N Baker A. R. grade hydrochloric acid. Copper introduced into the sample was computed to be < 0.5 n.mole ℓ^{-1}. The undiluted acid was examined by making standard additions to a seawater sample (pH ∿ 2.0); no peak height increase was found for several additions indicating that, under the test conditions, any copper contamination due to acid addi-

tions to samples was less than 0.3 n.mole ℓ^{-1} (<0.02 μg ℓ^{-1}). The same stock reagent bottle was used to prepare all acid additions to all samples.

Approximately three hundred samples have been collected and handled in the above fashion. Some measure - albeit a qualitative one - of confidence in the data set obtained was the reproducibility of the general shape of the copper depth profiles obtained from stations within this fjord and the narrow concentration range that the majority of samples fell within (following chapter). This suggests that contamination from random sources has been minimized (had it been prevalent, scatter in the data would be expected). The concentrations (following chapter) found were also compatible with some of the more recent copper data in the literature. There has recently been introduced a 10 ℓ 'drop top' Niskin bottle for trace metal sampling, which has an external closing mechanism and can be fitted to a pressure line such that samples may be filtered directly into the desired sample containers. The method is currently being used in the NOAA/BLM OCS (Outer Continental Shelf) study of the Gulf of Alaska. Concentrations of copper obtained from the adjacent Gulf of Alaska collected with this sampler were comparable with concentrations found in Resurrection Bay.

Seawater Storage

Because of the frequency at which samples were collected in this study (∿ 1 month), it was often necessary that samples be stored prior to analysis; some for about four months. Several samples were set aside frozen for analysis at different times and these data are shown

in Figure 12 and indicate that no significant losses to container walls or leakage of copper from the container body occurred when samples were stored acidified (pH ∿ 2.5) and frozen.

Interstitial Waters

Sediment cores were obtained with a Benthos gravity corer fitted with a ∿ 8' x 3.5" diameter polycarbonate core barrel. Cores were collected both with and without a stainless steel core catcher. There were no marked concentration differences detected in interstitial waters from cores collected either way indicating that the core catcher used did not contaminate the sample. The core was extruded into Reeburgh (1967) type squeezers that were fitted with nylon mesh screens and Nuclepore (0.4 μm) filters. The sediment squeezers were suspended vertically and several milliliters of fluid were extruded by squeezing under about 20 psi with nitrogen gas. A secondary filter (0.4 μm x 12 mm dia) was fitted to the squeezer outlet and about 20 mls of interstitial water collected directly into a 1/2 oz polyethylene bottle containing about 0.25 ml of ∿ 4N hydrochloric acid. Extrusion of samples directly into acid was found necessary to prevent the precipitation, upon standing, of red-brown particles, probably iron hydroxides. The sediment sample contacted the atmosphere only during the brief period of transfer from the core to the sediment squeezer and did not at any stage contact any metallic parts.

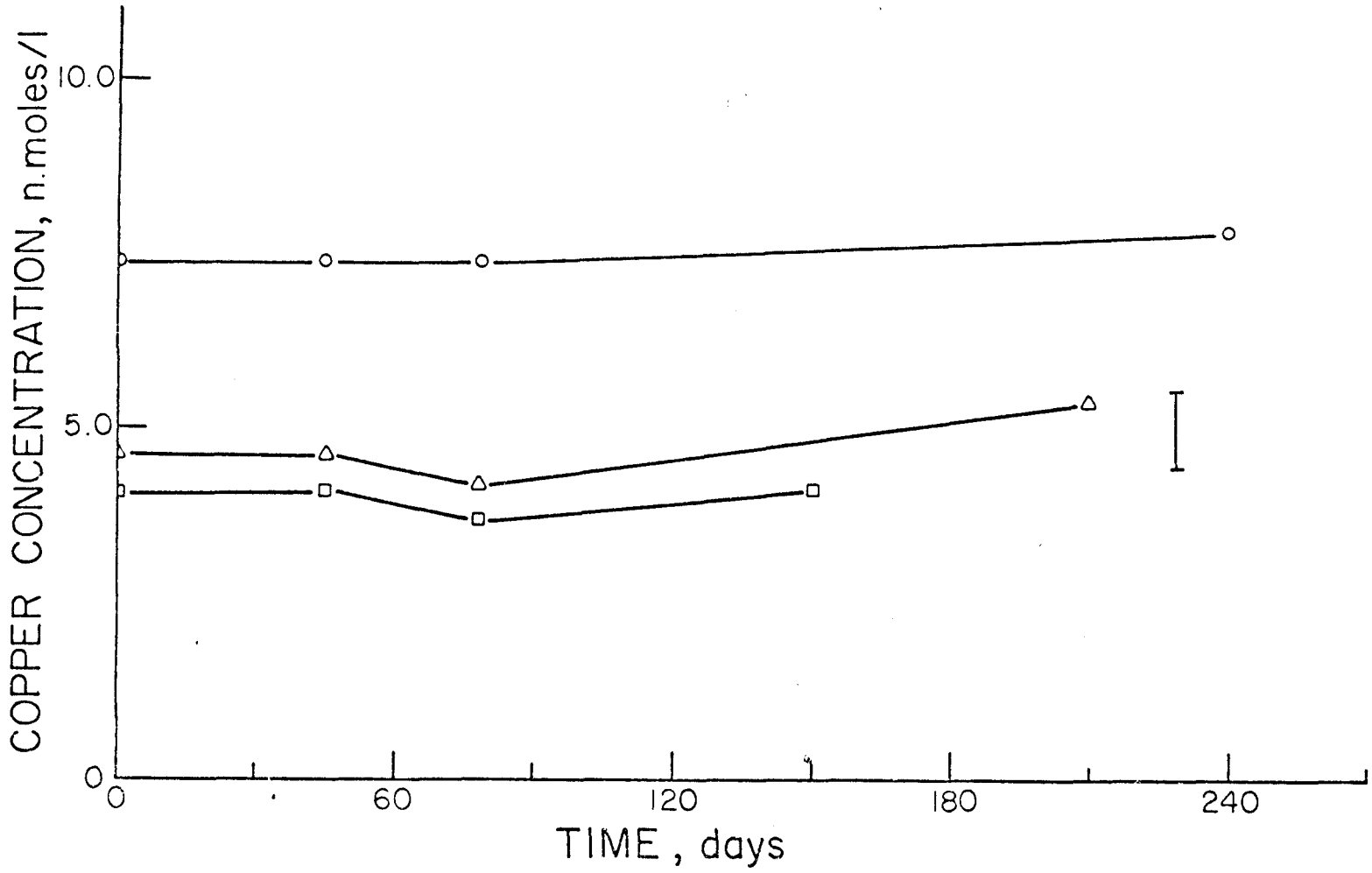


Figure 12. Effect of storage on copper concentrations of seawater samples (pH ∿2.5) in polyethylene bottles.

IV. SEASONAL AND SPATIAL VARIATIONS OF COPPER IN THE WATER COLUMN AND INTERSTITIAL WATERS OF RESURRECTION BAY.

Approximately 300 samples have been collected and analyzed for copper from four stations in this fjord during a two year period. Two stations were sampled in detail and represented respectively variations in the outer reaches of the fjord (Res-4) and the inner deep basin (Res-2.5). Other stations (Res-2, Res-3) were sampled in less detail but data from these verified that the changes observed at Res-2.5 were representative of that inner basin. The copper data presented should be considered in conjunction with the fjord hydrography discussed in detail in Chapter 2.

RESULTS

Water Column

Filtered Acidified Samples: 'Soluble' Copper

Copper concentrations determined in filtered (0.4 μm) Nuclepore and acidified (pH 2.0 to 3.0) seawater samples varied between 0.15 μg ℓ^{-1} (2.3 n.mole ℓ^{-1}) and 3.13 μg ℓ^{-1} (49.3 n.mole ℓ^{-1}). A histogram plot of all filtered samples is shown in Figure 13a; the mean concentration is 0.50 μg ℓ^{-1} (7.5 n.mole ℓ^{-1}). Histogram representations of the data from Res-2.5 and Res-4 are shown in Figures 13b and 13c. The mean concentration at Res-4 is statistically (95% confidence; log-transformed data and Z statistic) different, and greater than, the mean concentration at Res-2.5.

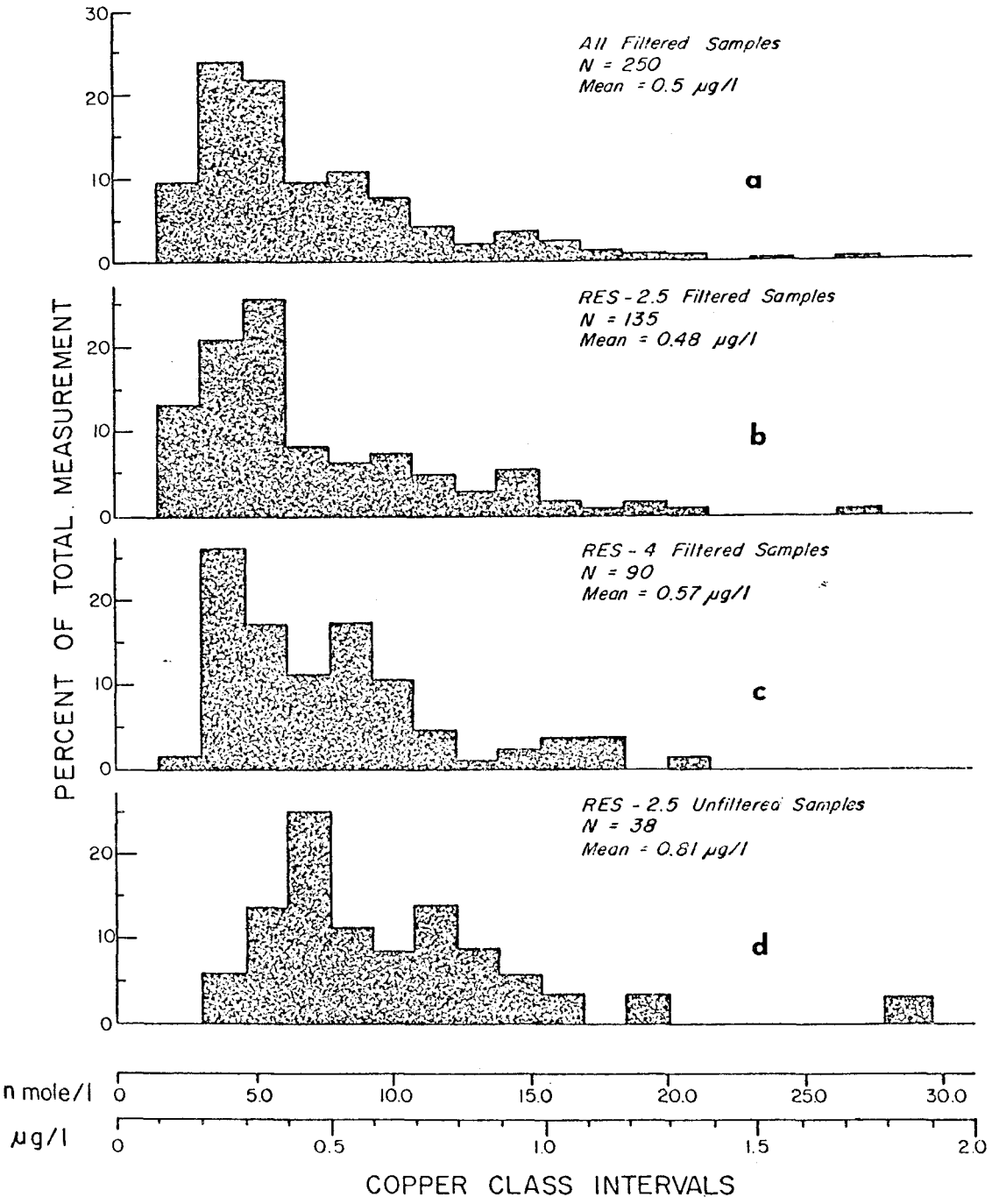


Figure 13. Histogram representations of copper concentrations from all acidified (pH ∿2.5) samples from Resurrection Bay.

Outer fjord: Summer and winter data: The concentrations of copper at Res-4 varied between 3.13 μg ℓ^{-1} (49.3 n.mole ℓ^{-1}) and 0.17 μg ℓ^{-1} (2.7 n.mole ℓ^{-1}) and are consistent with the range observed in the adjacent Gulf of Alaska (D. C. Burrell, personal communication). The depth variations of copper at Res-4 are shown in Figures 14 and Appendix C, Figure 1. The only trend in these data is that the surface water concentrations during oceanographic summer (June through October) are higher than during the oceanographic winter months (October through April). The depth profiles indicate both maxima and minima which appear at various depths and various times and probably reflect the advection of water masses through the outer region of the fjord. The time distributions - particularly below 150 m depth - show erratic variations; temperature, salinity and oxygen behave similarly (Chapter 2). Variations in copper concentrations in the outer reaches of the fjord therefore appear to be controlled principally by the rapidly changing oceanographic conditions at the coastline and exchanges with the adjacent Gulf of Alaska. The resolution of concentration changes due to non-conservative behavior in the water column, or exchanges across boundaries was not possible from these conditions.

The depth and seasonal distributions at Res-2.5 (Figs. 15 and Appendix C, Fig. 1) in the inner basin however show consistent variations that permit chemical reaction effects and exchanges across boundaries to be resolved from concentration changes due to physical transport phenomena. A continuous set of data has been obtained between April 1974 and May 1975 (Fig. 15) that encompasses the time period of

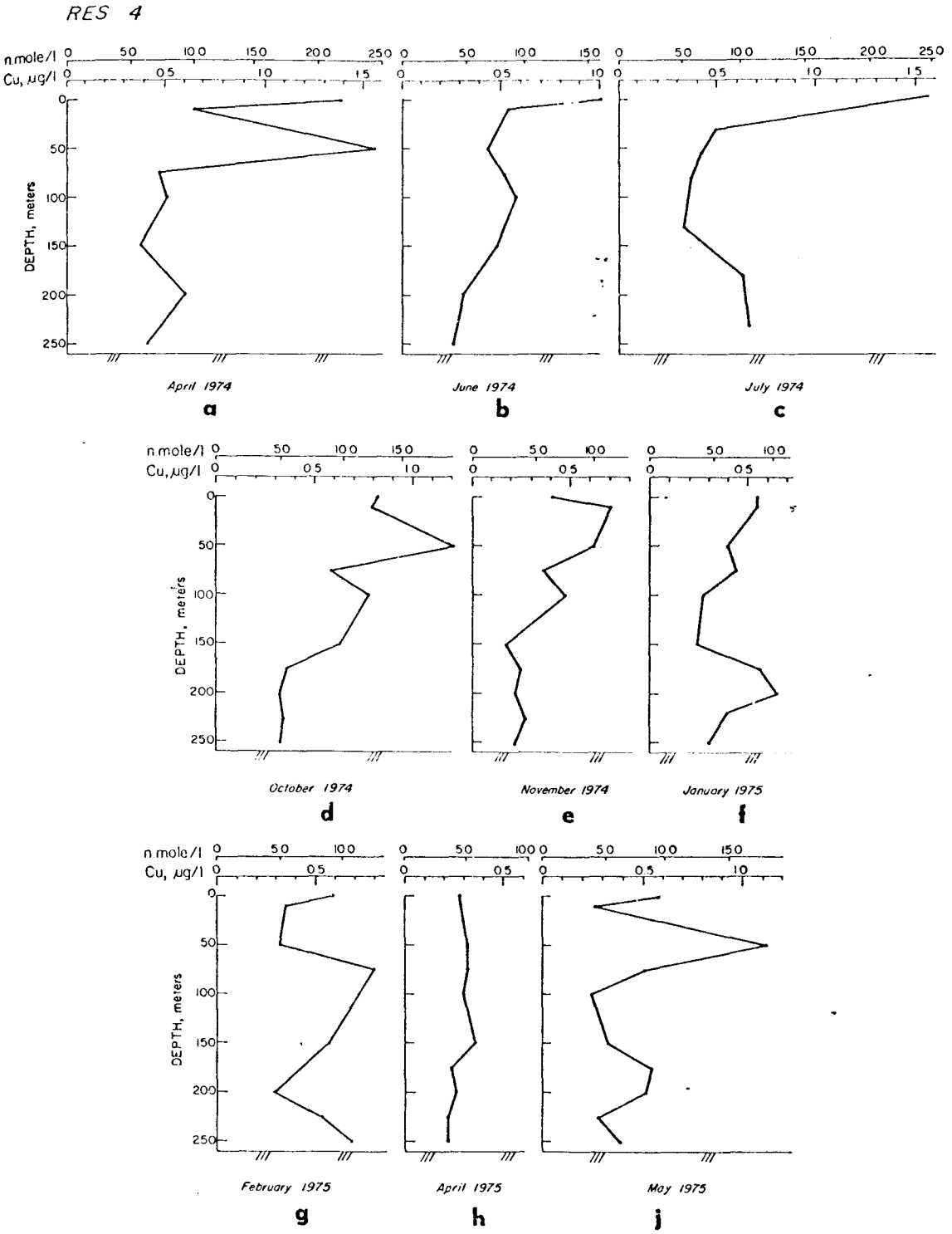


Figure 14. Depth distributions of copper at Res-4 between April 1974 and May 1975.

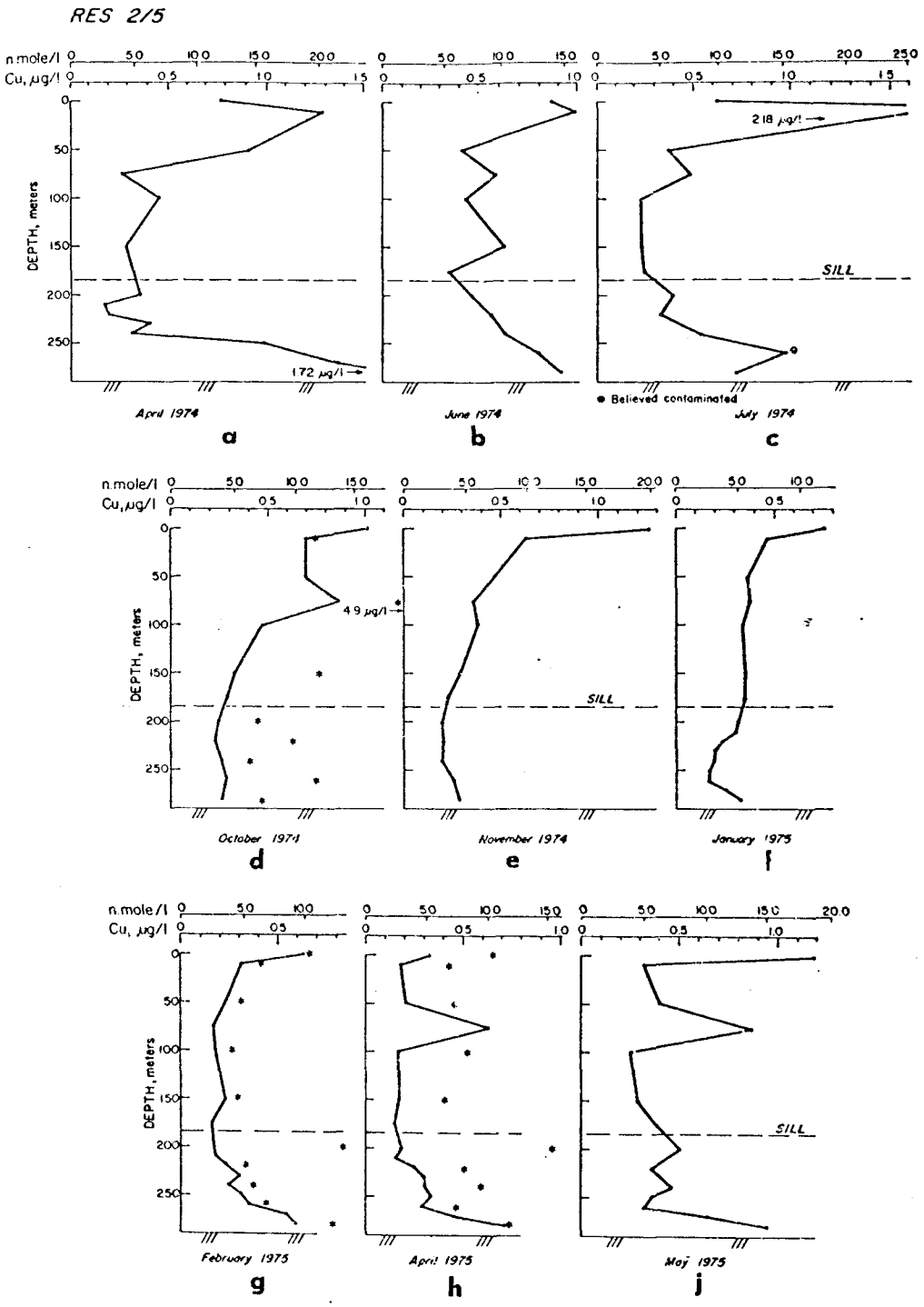


Figure 15. Depth distributions of copper at Res-2.5 between April 1974 and May 1975 (the starred dots represent copper concentrations in unfiltered and acidified samples).

advective renewal (summer) of the basin and of diffusive exchange with overlying waters (winter). The depth profiles are consistently concave down with a maximum at or near the sea surface, indicating year round transfer of copper from surface waters into the intermediate and deep waters.

Inner fjord: Summer data. Examination of the seasonal distributions of temperature and salinity in the inner basin (Chapter 2) shows that the basin water was replaced each summer and fall by advection of more dense water from the Gulf of Alaska. During extensive basin water renewal e.g., September-October, densities in the basin were identical to the densities found in a narrow depth range around the sill at the outer station (Res-4). Similarly the copper concentrations in the basin were identical to those in the same density range at the outer station. For example during 1973 extensive and apparently near continuous basin water renewal was occurring during September. The copper concentrations at Res-2.5 below about 200 m varied between 0.68 μg ℓ^{-1} and 1.01 μg ℓ^{-1}. This latter concentration range was found at Res-4 between depths of 150 m and 186 m (Appendix C, Fig. 1), encompassing the depth range of the densities found, below sill depth, in the inner basin. Similarly, the data from October 1974 during advective exchange showed concentrations between 0.23 μg ℓ^{-1} and 0.29 μg ℓ^{-1} below 180 m depth at Res-2.5 (Fig. 15d). At Res-4, the depth range over which the densities below sill depth at the inner station were found, was 184 to 230 m and the copper concentrations were

0.27 μg ℓ^{-1} to 0.29 μg ℓ^{-1} (Fig. 14d). The copper concentrations below about 150 m depth during the near continuous advective renewal of the deep water of the inner basin therefore reflected the copper levels of the source water.

The hydrographic data from May of 1975 indicated advection into the basin; approximately 90% of the basin water was replaced. Copper concentrations in the basin varied between 0.35 μg ℓ^{-1} and 0.95 μg ℓ^{-1}; the highest concentration being found at 280 m, (Fig. 15j). The concentrations of copper at Res-4 over a density range (26.08-25.85 closely encompassing the densities of the incoming water) varied between 0.56 μg ℓ^{-1} and 0.40 μg ℓ^{-1} between 175 and 215 m (Fig. 14j), and these latter concentrations approximate the concentrations measured between 180 and 260 m (0.33 μg ℓ^{-1}-0.50 μg ℓ^{-1}) at Res-2.5 in the inner basin.

Between April 1974 and the end of June 1974, approximately 40% of the basin water was replaced by advection across the sill; the influx that took place prior to the 28 June cruise penetrated to 270 m. Another influx occurred between June and July of 1974 that amounted to about 20% of the basin volume. The gradient in the bottom waters persisted throughout these partial advective replacements, (Fig. 15a, b, c) although between June and July of 1974 generally lower concentrations of copper, except in surface waters, were found throughout the water column. The gradient directed away from the sediments is dissipated as exchange across the sill becomes more extensive and frequent. The latter was nearly continuous by about September and copper concentrations in the basin were identical to the source water concentrations (discussed previously).

Inner fjord: Winter data. During the winter months, the water in the basin remains isolated from a free exchange with the Gulf of Alaska and exchanges predominately with the waters above the sill by turbulent mixing processes. Copper-concentration depth profiles remain concave down, but surface water mid-winter concentrations of copper are less than those during the summer months, suggesting decreased supply of copper to surface waters in the winter months. Copper concentrations, below sill depth, during the winter are determined, not principally by advective exchange across the sill (summer conditions), but by diffusional exchange across the sill, reactions in the water column and exchange across the sediment-seawater interface.

Subsequent to the advective exchange prior to October 1974 the November data (Fig. 15e) showed lower copper levels throughout the water column than in October; but a gradient was developing at the basin floor. Lower concentrations still (<0.2 μg ℓ^{-1}) were found in the deeper parts of the basin (220 to 260m) in January, but the concentration at 280 m increased somewhat, and the gradient directed away from the sediment was enhanced over the previous month (Fig. 15f). Compared to the November data, there was a general increase in the copper levels between about 140 and 220 m, which was inconsistent with the generally lower concentrations found throughout the remainder of the water column. This observation suggested a local source, or advection of water horizontally across the sill having a higher copper concentration than the resident water. Inspection of the density profile at Res-2.5 showed a higher density between about 100 and 165 m than during November, which

indicated the horizontal advection of a water mass from the outer regions of the fjord into the inner fjord across and above the sill. The advection is also reflected in the longitudinal temperature plots (Fig. 2, Appendix A). Inspection of the copper profile at Res-4, January 1974 (Fig. 14f) indicates the presence of a core of water between about 160 and 220 m with copper concentrations of between 0.35 μg ℓ^{-1} and 0.64 μg ℓ^{-1}. The densities of this water, (σ_t ∿25.34 to 25.65) were higher than the densities at the inner station during November between about 160 and 190 m. The core could have penetrated the intermediate levels of the fjord, but not below about 190 m between November and January. The increases observed in the intermediate waters and below the sill to about 220 m at Res-2.5 in January probably result from the horizontal advection of the higher copper concentration core of water into the inner fjord and dissipation *via* horizontal and vertical diffusion. At the end of February, still lower concentrations were observed throughout most of the surface and intermediate waters, but in the deep water the gradient directed away from the bottom waters was enhanced (Fig. 15g). Similarly, the April observations show lower levels of copper throughout the surface and intermediate waters, except for a maximum at 75 m, and the concentration of copper at the bottom (280 m) has increased since February and the gradient directed away from the sediments enhanced still further (Fig. 15h).

The profile at Res-2.5 measured in April 1974 (Fig. 15a) is consistent with that determined in April 1975 (Fig. 15h). Low concentrations ∿0.3 μg ℓ^{-1} of copper were determined in the intermediate waters;

particularly noticeable is the gradient directed away from the sediments in the bottom waters, indicating that similar processes were occurring in the deep waters of the inner basin during the winter of 1973-1974.

Unfiltered Acidified Samples: 'Particulate' Copper

Samples of seawater were collected on several cruises that were acidified but not filtered; particulate material was therefore retained. These samples upon analysis yield copper concentrations that include 'particulate' copper i.e., copper released from particles upon acidification and 'soluble' copper. These data are shown in Figure 15 with asterisks. The copper concentrations were higher in all samples measured this way than in filtered samples collected from the same depths. These data indicated that about 40% of the total copper measured ('particulate' plus 'soluble') was associated with particulate matter in the water column. The mean concentration of unfiltered samples (Fig. 13d) was (0.81 μg ℓ^{-1}) and was statistically, (95% confidence; log-transformed data; Z statistic) greater than the mean concentration (0.48 μg ℓ^{-1}) of filtered samples (Fig. 13b).

Interstitial Waters

A composite plot of the depth distributions of copper concentrations in sediment pore waters (samples filtered 0.4 μm Nuclepore, acidified pH∿2.0) obtained from six cores sampled over an eleven month period are shown in Figure 16. All interstitial water data are listed

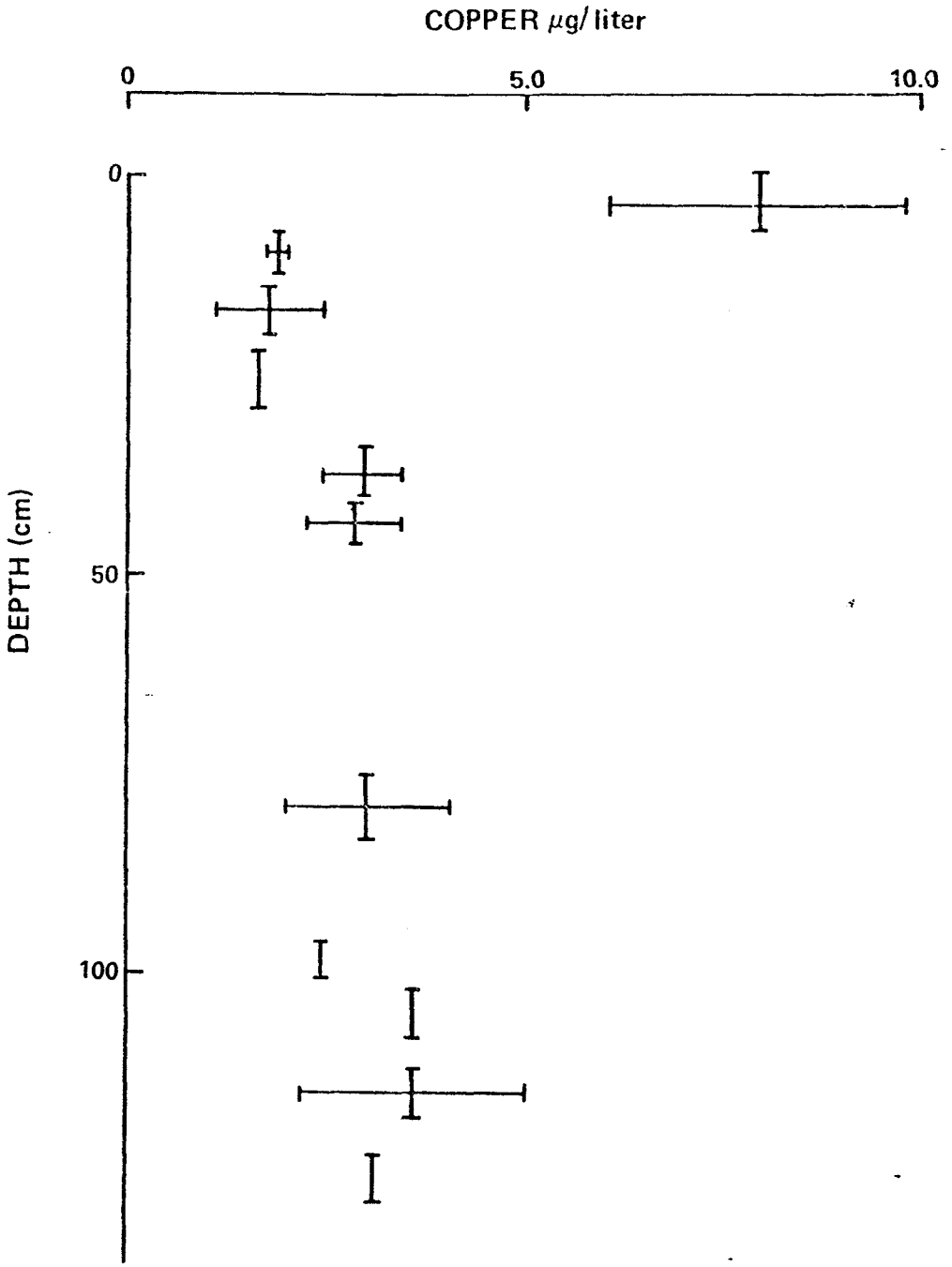


Figure 16. Composite plot of depth distributions of copper in interstitial waters; cores collected July 1974 through May 1974 (the horizontal bars represent one standard deviation of the concentrations measured).

in Appendix C, Table 1. Although there is some variability in concentrations between cores all depth distributions are identical. Two significant features emerge from these data.

(1) Maximum copper concentrations were always found in the surface segment (0∿7 cm) and varied between 4.90 μg ℓ^{-1} and 9.98 μg ℓ^{-1}. Concentrations abruptly decreased below about 7 cm depth.

(2) Minimum concentrations were found in a relatively narrow segment, 7 cm through 20 cm depth, of the sediments; below about 20 cm depth copper concentrations increased to between 3 μg ℓ^{-1} and 5 μg ℓ^{-1} at about 130 cm depth.

The raw sediment segments from which the interstitial water was squeezed did not smell of free H_2S, and measurements made by the method of Cline (1969) found no free hydrogen sulfide in any interstitial water segments. However, when a little dilute hydrochloric acid was added to the raw sediments, H_2S was freely emitted except from the very surface segment. The observation indicates that the surface segments (<10 cm) are oxidizing but immediately below are reducing and sulfides formed by the reduction of sulfate are precipitated. The distribution of nitrate in the interstitial waters (Heggie *et al.*, 1977) also indicates anoxic conditions below about 10 cm depth. Highest nitrate concentrations were found in the surface segment, but immediately below were reduced to undetectable levels indicating denitrification which proceeds only under anoxic conditions.

Sediments

Copper, iron and manganese concentrations were measured in the sediments of Resurrection Bay by the method of Chester and Hughes (1967). The authors state that a combined acid-reducing agent solution will selectively dissolve ferromanganese minerals and associated iron oxides, carbonate minerals and adsorbed trace metals from pelagic sediments, but clay minerals were not attacked by the reagent. With respect to Resurrection Bay sediments, the fraction of copper measured by this method was not investigated but under the acid conditions (pH <2) trace metals associated with organic matter and solid sulfide phases would be expected to be released; however to what extent remains unknown. The data are shown in Table 13, and indicate, upon burial, insignificant losses of copper and iron from the 'extractable' sediment fraction. Manganese however does show significant losses from the 'extractable' fraction upon burial which may be explained by the diagenetic solubilization and remobilization of manganese (Lynn and Bonatti 1965; Calvert and Price, 1972). The data suggest that the geochemistry of copper in the sediments more closely resembles that of iron than of manganese.

Resurrection River Runoff

The principal pathway by which copper is added to the oceans is continental weathering and runoff in rivers (Goldberg, 1975). Measurements of copper in filtered and acidified (pH $\sim$ 2.0) freshwater from the Resurrection River were made to compare them with surface and near-

TABLE 13

Manganese, Copper and Iron Concentrations on Sediments
(Method: Chester and Hughes, 1967)

Depth in sediment (cm)	Manganese mg kg^{-1}	Copper mg kg^{-1}	Iron mg kg^{-1}
0 - 0.5	4072 ± 158	21.3 ± 3.4	19274 ± 1347
0.5- 5.0	1021 ± 30	21.2 ± 1.3	19012 ± 1221
6.5-12.5	345 ± 13	21.8	19095 ± 1007
14.2-22.0	290 ± 3	23.4	17557 ± 2401
42.0-47.5	316 ± 10	21.9	19021 ± 604
76.0-83.5	302 ± 42	21.3 ± 1.8	17891 ± 765

The statistic shown is the standard deviation of duplicate samples.

surface copper concentrations in the fjord. The data are shown in Table 14. The concentrations, although few in number, were consistently less than the concentrations measured in near- and surface waters at the inner station, Res-2.5. However, the copper depth profiles within the fjord were persistently concave down with a maximum either at or near to the sea surface. This latter can mean that copper is added to the fjord waters proper *via* the surface waters. Release of copper from the solid phases has to be invoked to explain the persistent maximum near the interface and higher concentrations in near surface fjord waters compared to river water concentrations. The two most likely sources are particulate input, across the air-sea interface, or from the Resurrection River. It has not been possible, and it was not intended to evaluate these, but in the relatively small areal confines of a fjord the latter is probably quantitatively most important.

DISCUSSION

Water Column

Seasonal Concentration Variations and Fluxes of 'Soluble' Copper

The following facts may be extracted from the foregoing water column seasonal concentration variations and depth distributions.

1. A maximum copper concentration was always found at or near the sea surface. A persistent concave down profile through the surface and intermediate waters of the inner basin can only indicate supply of copper to the deep fjord waters.

TABLE 14

Copper in Resurrection River

(Samples filtered 0.4 μm and acidified pH ∿2.0)

Month	Copper μg ℓ^{-1}
October 1974	0.16
	0.12
	0.43
	0.36
March 1975	0.09
	0.06
April 1975	0.08
	0.05
May 1975	0.64
	1.03
	0.96
September 1975	0.25
	0.24

2. The average 'soluble' copper concentration of the source waters (Res-4) for the fjord was greater than the average concentration of the waters within the inner basin (Res-2.5).
3. 'Soluble' copper concentrations in intermediate and deep waters of the inner fjord decreased throughout the summer and early winter months (June through January).
4. A concentration gradient directed away from the sediments developed during the early winter months (October-January) and was enhanced during the winter and spring months (February-April). The gradient persisted throughout the early advective exchanges (May-July) through the basin during the following summer.
5. The concentrations of all unfiltered samples were higher than the concentrations of filtered samples collected concurrently at the same depths.

The relative isolation of the inner fjord, and in particular the deep basin, permits the development of gradients and losses or gains from the water column by chemical or biological phenomena to be preserved and not masked by rapid advective exchange. The time series of observations permits the rates of the losses or gains mentioned above to be computed. A budget equation for copper in the water column of the deep inner basin, below sill depth, may be written:

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta Cu}{\delta t}\, dZ = \{Cu_{(I)} - Cu_{(E)}\} \frac{1}{\Delta t} \int_{o}^{h} dZ - \int_{\text{bottom}}^{\text{sill}} \frac{\delta}{\delta Z}\left(K_z \frac{\delta Cu}{\delta Z}\right) dZ + \int_{\text{bottom}}^{\text{sill}} J\, dZ \qquad (4.1)$$

The equation is similar to that written earlier for the oxygen budget (Chapter 2), but Cu represents a copper concentration. The equation states that the observed rate of change of copper in the basin is a balance between advective and diffusive fluxes and a zero order source and/or sink term (J). The advective contribution was neglected when additions of water across the sill into the basin were not observed. If J is negative it represents a 'removal' rate and conversely, if positive a 'remobilization' rate. The computed J is the net result of input and export contributions integrated and averaged between the sill and bottom depths. J may be specific, i.e., due to a single input or export reaction, or be the result of opposing input and export reactions operating at different depths, between the limits of the integration. If the latter is the case, complete resolution of J requires the independent determination of one of the contributing terms. Table 15 lists the computed J in sign and magnitude in the copper budget for various times of the year. The details of calculations of these types are given in Appendix C.

The results show net losses of copper from the water column (bounded by the sill and the basin floor) during the summer and early winter months (June-January) at rates of between -9.1 and 2.6 μg Cu cm^{-2} yr^{-1}, (-0.91 and 0.26 μg Cu ℓ^{-1} yr^{-1}) mean = 5.5 μg Cu cm^{-2} yr^{-1}, (0.55 μg Cu ℓ^{-1} yr^{-1}). Data in Figure 15 indicate that, in the absence of advective influxes into the fjord, copper concentrations also decrease in intermediate depth ($\sim$ 100-200 m) waters. Assuming that removal processes operate throughout all of the water column the net (but

TABLE 15

Rates of Change of Copper through the Deep Waters (sill-bottom) of Resurrection Bay

Observation	Rates	
	Integrated (J·dZ) μg Cu cm^{-2} yr^{-1}	Average (J) μg Cu ℓ^{-1} yr^{-1}
21 April 1974	+1.9 (1.2-2.6)*§	+0.19 (0.12-0.26)
28 June 1974	-9.9 (12.4-7.3)*†	-0.99 (1.24-0.73)
25 July 1974	Successive advective replacement of deep water	
18 October 1974	-4.1 (3.1-5.5)†	-0.41 (0.31-0.55)
26 November 1974	-2.6 (1.5-3.6)†	-0.26 (0.15-0.36)
21 January 1975	+9.1 (9.9-8.4)§	+0.91 (0.99-0.84)
27 February 1975	+3.3 (2.4-4.2)§	+0.33 (0.24-0.42)
9 April 1975	+3.9 (0.3-7.5)*§	+0.39 (0.03-0.75)

* Include contributions from advective influx across sill.

† Mean of net losses, 5.5 μg Cu cm^{-2} yr^{-1}, (0.55 μg Cu ℓ^{-1} yr^{-1})

§ Mean of net increases 4.6 μg Cu cm^{-2} yr^{-1}, (0.46 μg Cu ℓ^{-1} yr^{-1})

neglecting river supply) integrated removal flux of copper from the total water column was estimated to be 16.5 μg Cu cm^{-2} yr^{-1}. During the winter and spring months copper increases in the deep basin at rates varying between 9.2 and 1.9 μg Cu cm^{-2} yr^{-1}, (0.92 and 0.19 μg Cu ℓ^{-1} yr^{-1}), mean = 4.6 μg Cu cm^{-2} yr^{-1}, (0.46 μg Cu ℓ^{-1} yr^{-1}).

Mass Balance Between Overlying Waters and Surface Sediments

The seasonal development of a gradient directed away from the sediments, together with the observation of concentrations of copper in the upper 5 to 10 cm of interstitial water of about one to two orders of magnitude higher than those in the overlying water indicate that the surface sediments are a source of copper for the fjord bottom waters and that copper is returned into the overlying waters. A copper maximum at the sediment-seawater interface (Fig. 16) indicates copper diffusion both down into the sediment and up into the overlying water. The deep, >10 cm depth sediments will be considered later, and only the effects of the surface sediment as a control on the overlying water concentrations will be considered at present. The mean net rate at which copper was found to increase in the overlying water (0.46 μg Cu ℓ^{-1} yr^{-1}) would, if it is assumed that the increase is solely from the sediment, be sufficient to deplete a surface 7-cm segment of interstitial water of copper (mean concentration 8 μg ℓ^{-1}) in less than ten days. The surface maximum in the interstitial waters persisted at least over about a 12-month period (Fig. 16). The lowest concentration observed in the top segment of interstitial water was 4.90 μg ℓ^{-1}. A

mass balance argues that some mechanism must be operating to maintain the maximum, and the high concentrations, at the sediment surface in the face of significant losses from it into the overlying water. A source of copper needs to be found to maintain supply to the interstitial waters. Interstitial water data show that copper is not supplied to the surface segment from deeper within the sediments. Copper concentrations on sediment were found to be about 20 mg kg^{-1} (Table 13); about three orders of magnitude higher than the interstitial water concentrations. A remobilization of copper from sediment particles at the sediment-seawater interface must be invoked to explain the high concentrations and persistent maxima in surface interstitial waters. A supply of particulate material to the surface sediments from deep within the sediments is unlikely. Sediment reworking by burrowing benthic organisms serves to increase a particles residence time in surface sediments but a net transport of sediment upward is impossible. Because of nitrate depletion below about 10 cm depth, indicating denitrification in sediments which proceeds only under anoxic conditions, irrigation of sediments by benthic organisms can only be effective to about 10 cm depth. It is therefore proposed that copper is carried to the sediments by particles falling through the water column of the inner basin. The following information supports this hypothesis.

(1) A higher 'soluble' copper concentration for the fjord source waters suggests a loss of copper from waters within the inner basin.

(2) Significant decreases in the 'soluble' copper concentration of the intermediate and deep waters of the inner fjord were evident (Fig. 15) during the summer and early winter months. A net loss of

copper was found from deep waters of the inner basin (Table 15).

(3) About 40% of the total copper (unfiltered acidified samples) measured in the water column was associated with particulate matter.

The copper carrying capacity of suspended material is considered in more detail below and an estimate of the rate at which copper is transported to the sediments is developed.

Particulate Flux of Copper through the Water Column

The nature of suspended particulate matter in seawater is complex and at any given location is likely to be a 'mixed bag' aggregate of inorganic and organic fractions, e.g., clay minerals, mixed oxides and hydroxides of iron, manganese and aluminum and organic matter derived from terrestrial sources or produced *in situ* such as plant and animal remains, fecal pellets and bacteria. The data in Figure 15, indicate that copper in Resurrection Bay is associated with suspended particulate matter. A particulate flux of copper may be calculated if the following are known; the concentration of suspended particulate material in the water column, the concentration of copper on suspended material (i.e., mass of copper per unit mass of particulate material), and a settling velocity for the suspended material.

$$\begin{array}{l}\text{Particulate copper transport} \\ \mu g\ Cu\ cm^{-2}\ yr^{-1}\end{array} = \begin{array}{c}\text{Suspended particulate matter concentration} \\ mg\ cm^{-3}\end{array} \times \begin{array}{c}\text{Copper on particulate matter} \\ \mu g\ Cu\ mg^{-1}\end{array} \times \begin{array}{c}\text{Particulate matter settling velocity} \\ cm\ yr^{-1}\end{array} \qquad (4.2)$$

Assuming that the copper content of the suspended particulate matter is acquired from the water column, that removal is rapid with respect

to the settling velocity, and that all particulate material reaches the sediment surface, then the flux of copper to the sediment is directly proportional to the settling velocity of the particles.

The concentration of copper on particulate matter was calculated at each sample depth by dividing the difference between unfiltered and filtered sample concentrations i.e., 'particulate' copper by the concentration of particulate material at that depth:

$$\text{Copper on particulate matter } (\mu g\ Cu\ mg^{-1}) = \frac{\text{Copper in unfiltered sample } (\mu g\ \ell^{-1}) - \text{Copper in filtered sample } (\mu g\ \ell^{-1})}{\text{Particulate matter concentration } (mg\ \ell^{-1})} \quad (4.3)$$

Only data collected during April of 1975 were complete in themselves to calculate a concentration computed this way, and from 10 data points an average concentration of 0.32 $\mu g\ Cu\ mg^{-1}$ (standard error = 0.07) was calculated from equation 4.3.

An alternate computation using data between October and April indicated that about 40% (30 data points) of the total copper measured was bound to particulate material, i.e.,

$$\text{Fraction of 'total' copper on/in particulate matter} = \frac{\text{Copper in unfiltered sample } (\mu g\ \ell^{-1}) - \text{Copper in filtered sample } (\mu g\ \ell^{-1})}{\text{Copper in unfiltered sample } (\mu g\ \ell^{-1})} \quad (4.4)$$

Assuming that the above percentage is representative at all 'soluble' concentrations then, at an average concentration of 'soluble' copper at Res-2.5 of 0.48 $\mu g\ \ell^{-1}$ (Fig. 13b) an average concentration of 'particulate' copper of 0.33 $\mu g\ \ell^{-1}$ was calculated using equation 4.4. The average suspended load in Resurrection Bay was 1.03 $mg\ \ell^{-1}$ (standard

error = 0.11 mg ℓ^{-1}, 30 samples) and these data combined in equation 4.3, yield a concentration of copper on particulate matter of 0.31 µg Cu mg^{-1} (standard error = 0.15). This latter compares favorably with the previous estimate but the variance is increased when the result derived from equation 4.4 (30 data points) is extended to the larger sample population (135 data points, Figure 13b) via equation 4.3.

McCave (1974) has calculated settling velocities for different particulate size classes, assuming particles to be a 60:40 mix of mineral and organic matter. Measurements of suspended particle sizes were not made in Resurrection Bay, but a dominant range of particulate sizes in oceans and estuaries (Appendix C, Table 2) has been chosen between 1 and 50 µm, and this latter has been assumed applicable to Resurrection Bay. Settling velocities from McCave (1974, Table 2) for these sized particles ranged between 3.5×10^{-5} and 5.3×10^{-3} cm sec^{-1}. When combined with the average concentration of particulate material in the water column of Resurrection Bay (1.03 mg ℓ^{-1} 30 data points April-May) and the concentration of copper on particulate matter (0.32 µg Cu mg^{-1}) the range of particulate copper fluxes through the water column was calculated to be 0.4 to 55 µg Cu cm^{-2} yr^{-1}.

The flux calculations must be considered order of magnitude only, and would vary as the particulate load varied seasonally in the fjord. Because the average concentration of particulate material used in the calculation was from principally winter data the particulate copper flux estimates may be somewhat low. They do, however, span the observed range of copper losses from the deep (sill-bottom) water column

of; 9.9 to 2.6 μg Cu cm^{-2} yr^{-1} (Table 15), including an estimate of a mean net removal flux from the total water column of 16.5 μg Cu cm^{-2} yr^{-1}.

Potential Copper Transport by Different Particle Types

Introductory remarks. There are a variety of particles in seawater, both inorganic and organic, that may scavenge trace metals from the water column. However, in any given environment the relative importance of each in transporting trace metals to sediments is not easy to resolve. Throughout the following pages an effort is made, to evaluate which of three principal classes of particles - biogenic, manganese and iron oxides and hydroxides and silts and clays - is principally responsible for the removal of copper from the water column and subsequent transport to the sediments of Resurrection Bay. The evaluation will be made by utilizing actual, or approximations to the fluxes of each of the above particle types into the fjord, assuming that each particle type could be solely responsible for transport and that the concentration of copper on particles, 0.32 μg Cu mg^{-1}, is applicable to each particle type. The product of the particle flux and the concentration of copper on particles yields the copper flux to the sediment.

Copper transport by biogenic particulate matter. Plankton and animals can remove trace metals from seawater *via* direct uptake and incorporation into body structures, or by surface adsorption onto cell and

body exteriors. Trace metals so accumulated consequently sink with the detritus and this latter may further passively accumulate trace metals from the water column as it sinks. Phytoplankton that have accumulated trace metals either by adsorption or direct uptake, and which escape grazing, sink beyond the euphotic zone and become subject to bacterial decay such that oxidized forms of nutrients (N, P, Si) are released to the water column. The relative importances of potential release of copper to, versus scavenging from, the water column as a result of the change in character of the particle during transport down and oxidation could not be adequately evaluated from the data set and remains unknown.

A descriptive examination of the similarities and differences between the seasonal and depth variations of the nutrients and copper in Resurrection Bay is given in Appendix C: a brief summary follows. Surface water summer distributions indicate that net removal processes control nutrient concentrations (Heggie *et al.*, 1977). However, for copper, net supply dominates over net removal in surface waters. The decreased concentrations of copper in the water column below the euphotic zone during summer and early winter months, and the persistent concave down distributions can only be explained by removal processes, operating in the deeper fjord waters. In contrast, decreased nutrient levels below the euphotic zone during the winter months result principally from vertical mixing processes which replace the nutrient depleted surface waters. Nutrients (N, P, Si) are 'remineralized' in the surface sediments and returned to the overlying fjord waters (highest concentrations in surface and near interstitial waters, gradients

between interstitial waters and overlying water column); 'remineralized' nutrients originate from the degradation of particulate biological material. A mass balance for copper between the surface sediments and overlying waters (discussed previously) indicated that copper was 'remobilized' from particulate phase(s) in surface sediments and returned to the overlying fjord waters. It is implied from these data that copper and nutrients undergo, at least in part, similar processes in surface sediments. An estimate of the biogenic flux of copper to the sediment follows.

The potential flux of copper to the sediment surface by biogenically derived material relys principally upon the following; primary productivity in Resurrection Bay, the rate of oxidation of particulate organic matter in the ocean and a Cu:C ratio in phytoplankton. The calculation assumes that copper is associated solely with biogenic particulate matter, although it does not distinguish between copper actively taken up and that passively collected onto the exterior of particles. The primary productivity determines the *in situ* carbon flux through the water column; no account is taken of other particulate organic matter sources. Carbon oxidized within the water column is accounted for and subtracted from the primary productivity to yield the particulate carbon flux to the sediment. A general model for the biogenic carbon flux is first examined for Resurrection Bay and then used to compute the copper flux, *via* utilization of a generalized Cu:C ratio for phytoplankton.

The biological oxidation of particulate organic material with depth in the ocean may be expressed by the following general equation (Wyrtki, 1962; Broenkow, 1969):

$$R = R_o \, e^{-\alpha z} \tag{4.5}$$

where: R_o = rate of oxidation at any given depth and is proportional to the concentration of oxidizable particulate material

z = depth, positive downward

α = $\dfrac{\text{rate of oxidation of particulate organic matter}}{\text{net rate of transport downward}}$

For any basin of finite depth the flux of particulate organic material that reaches the sediment floor can be computed by integrating the above equation and subtracting the result from the primary particle flux:

$$F = P - \int_o^h R_o \, e^{-\alpha z} \, dZ \tag{4.6}$$

where: F = flux of material reaching sediment surface

P = primary productivity rate in euphotic zone

h = depth of basin

R = rate of oxidation of particulate organic matter

The data which were utilized to determine values of R and α in Resurrection Bay are given in Appendix C.

The flux of carbon to the sediment surface of Resurrection Bay may be examined from a general solution to the above equation:

$$F \approx P - \frac{Ro}{\alpha} \, (1-e^{-\alpha h}) \tag{4.7}$$

All terms have been previously defined. Rates of primary productivity in Resurrection Bay varied between 19 and 2103 mg C m^{-2} day^{-1} (D. W. Boisseau, personal communication) during 1974-1975. A weighted mean for the spring and summer data (March 27-October 18) was 940 mg C m^{-2} day^{-1}. For values of R (biological carbon consumption in the water column) of 1.45 X 10^{-6} gm C cm^{-3} yr^{-1} and values of α between 3.4 X 10^{-4} cm^{-1} and 4.3 x 10^{-5} cm^{-1}, between about 30 and 80 % of the mean summer surface primary productivity may escape degradation in the water column and reach the sediments. The large uncertainty is due to inadequate knowledge of particle sizes, particle concentrations and particle settling velocities - mass flux downward - in Resurrection Bay. The particulate carbon flux to the sediments is probably high. Oxygen consumption rates used were for deep waters only. Oxygen consumption (proportional to particulate carbon concentration) ought to be higher in surface and intermediate waters, meaning that carbon oxidized in the water column would be increased. Also, carbon that is lost *via* grazing has not been accounted for. Assuming a net 20% loss of carbon fixed in surface waters to higher trophic levels the plant detrital flux to the sediment surface may be reduced to between about 70% and 25% (Appendix C) of the surface primary productivity.

The uncertainties in a calculation of this type are large, but the result - that a significant fraction of carbon fixed in surface waters sinks to the sediment surface where it is degraded - is supported by the interstitial water nutrient concentrations and concentration-depth profiles (Heggie *et al.*, 1977). Christensen and Packard (1976) computed,

from direct measurements that the respiratory activities of oxygen consuming organisms in the deep waters of another fjord (Dabob Bay, Puget Sound) were responsible for 36% of the summers primary productivity and that 15% (believed to be low) of the bottom water oxygen consumption was accounted for by benthic organisms.

The above calculations, in terms of carbon, were converted to a biogenic copper flux by utilization of a generalized Cu:C ratio in phytoplankton. Assuming that the particulate matter measured in Resurrection Bay was all plankton derived detritus and 20% carbon, a Cu:C ratio for this material (copper concentration 0.32 μg Cu mg^{-1}, p. 107) was computed to be 16×10^{-4}. This ratio differs from actual Cu:C ratios which have been reported, or which were calculated from various data reported in the literature (Appendix C, Table 3). Cu:C ratios in the latter table range between 0.4×10^{-4} and 3.2×10^{-4} (mean 1.8×10^{-4}). This variance indicates either enhanced incorporation of copper into/onto plant material in Resurrection Bay or, and most probably, an invalid assumption i.e., suspended matter contains an unknown proportion of abiotic copper carrying particles. The Cu:C ratio when combined with the range of carbon fluxes to the sediments during the summer months (660-230 mg C m^{-2} day^{-1}) yields a range of copper fluxes to the sediments of 38.5-13.4 μg Cu cm^{-2} yr^{-1}. Utilization of a more general Cu:C ratio of 1.8×10^{-4} (Appendix C, Table 3) or 0.18 μg Cu mg^{-1} C yields a range of copper fluxes to the sediments of 4.4-1.5 μg Cu cm^{-2} yr^{-1}. For a biogenic particle size of about 20 μm the carbon flux to the sediment surface was found to be 475 mg C cm^{-2} yr^{-1} and for a Cu:C ratio of 1.8×10^{-4} the copper flux to the sediments was 3.1 μg Cu cm^{-2}

yr^{-1}. Although the range of copper fluxes by biogenic particles is wide, the latter are of the same order as the estimated net removal rate from the water column (16.5 µg Cu cm^{-2} yr^{-1}, p. 103).

Copper transport by clay and silt sized particles - Sediment discharge data were obtained from the U.S.G.S. (unpublished data) and, using cumulative size distributions of sediment in Resurrection River freshwater runoff, and sediment discharge rates, the inputs of silt and clay sized particles to the fjord were computed. Assuming that there is no net accumulation in surface waters and no transport of these sediments out of the fjord, the flux of material to the sediment surface was computed by dividing the discharge rate by the surface area of the inner fjord basin. The flux of copper to the sediment was computed:

$$\begin{matrix}\text{Copper flux} \\ \text{to sediment} \\ \mu g\ Cu\ cm^{-2}\ yr^{-1}\end{matrix} = \frac{\text{Sediment discharge rate } (mg\ yr^{-1})}{\text{Basin surface area } (cm^{-2})} \times \begin{matrix}\text{Copper on} \\ \text{particulate} \\ \text{matter} \\ \mu g\ Cu\ mg^{-1}\end{matrix} \quad (4.8)$$

Use of the above concentration implies that the samples from which it was computed were all suspended clay and silt sized particles. The mean fluxes of copper carried on these latter particle types were computed to be 276 ± 206 µg Cu cm^{-2} yr^{-1} and 205 ± 123 µg Cu cm^{-2} yr^{-1}, respectively. The statistics quoted include variances associated with the sediment discharge rate and the concentration of copper on sediment. Although silt sized particles would be expected to be deposited rapidly and confined principally to the head of the fjord, clay sized particles may be transported great distances from their source. The net effect is to increase their residence time in the water column and these

calculations do not account for clays that may be transported beyond the inner basin of Resurrection Bay. This latter means that the net flux of clay sized particles to the sediment would be lower than that used in the computation, and the copper flux would be correspondingly reduced. Nevertheless, the calculations indicate that copper transports by clays and silt sized particles would be about fifteen times greater than the estimated removal flux from the water column (16.5 μg Cu cm^{-2} yr^{-1}); about 7% only of the actual clay and silt sized particles would need to be retained in the inner fjord to reduce the copper fluxes by these particles to approximate the estimated mean removal rate (16.5 μg Cu cm^{-2} yr^{-1}; p. 104).

Copper transport by iron and manganese particles. The concentrations in sediments of elements introduced into the oceans principally *via* continental runoff but which are removed from the water column generally decrease with increasing distance offshore. Manganese and iron precipitate directly from seawater (predominately as hydroxides and oxides) and settle to the sediment. These elements may also be transported down by associating with other particle types. Copper, however is apparently not precipitated from seawater and is transported to the sediments only *via* the latter mechanism. Assuming that copper is lost from the water columns of Resurrection Bay and the Gulf of Alaska solely *via* precipitating manganese and iron particles, and that the affinity of copper for these particles is the same in the fjord and the adjacent continental shelf, the fluxes of copper to the sediments would be proportional to the respective fluxes of iron and manganese

through the water columns of the fjord and the adjacent Gulf, and copper:scavenging-element ratios in the sediments would be identical in the Gulf and the fjord. Elemental concentrations and ratios in the Gulf of Alaska and Resurrection Bay are shown in Table 16, and indicate, if the above reasoning is valid, that neither iron nor manganese are solely responsible for the removal of copper from the water column. The copper:iron ratios are of the same order of magnitude but the copper:manganese ratio in Resurrection Bay is about one order of magnitude less than that in the Gulf; differences in diagenetic remobilization and re-precipitation of iron and manganese may contribute to these variances but the extent of this in either environment is not known.

Some concentration data for iron and manganese in the Resurrection River were available from the U.S.G.S (unpublished data). The mean iron and manganese ('particulate' plus 'soluble') concentrations were 100 $\mu g\ \ell^{-1}$ (standard error = 26.8, 26 samples) and 3.3 $\mu g\ \ell^{-1}$ (standard error = 2.0, 12 samples) respectively. These data were derived from only a few analyses, but they are in accord with data of Durum and Haffty (1963), who give the median concentrations of iron and manganese in North American rivers as 300 $\mu g\ \ell^{-1}$ (range 31 to 1679 $\mu g\ \ell^{-1}$) and 20 $\mu g\ \ell^{-1}$ (range 0 to 185 $\mu g\ \ell^{-1}$) respectively. The former data when combined with freshwater runoff rates of the Resurrection River provide an order of magnitude assessment of iron and manganese fluxes through the water column of the inner fjord basin. Assuming that all of the iron and manganese introduced by the river is lost to the sediments of the

TABLE 16

Manganese, Iron, and Copper Concentrations and Copper:Manganese Copper:Iron Ratios from the Surface ∿5cm Sediments of Resurrection Bay and the Gulf of Alaska

Element	*Resurrection Bay	#Gulf of Alaska
	Concentration mg kg^{-1}	
Mn	1,326 ± 915	95.3 ± 11.5
Fe	19,040 ± 176	4,660 ± 1166
Cu	21.2 ± 0.03	11.4 ± 0.88

Statistics are standard errors of weighted means

Cu:Mn	$1.6 \pm 1.1 \times 10^{-2}$	$1.2 \pm 0.17 \times 10^{-1}$
Cu:Fe	$1.1 \pm 0.08 \times 10^{-3}$	$2.5 \pm 0.36 \times 10^{-3}$

Statistics are standard errors of the quotients of weighted means

°Analyses, method of Chester and Hughes, 1967

*Duplicate analyses from a single core only

#Means of data from 16 samples analyzed in duplicate

inner fjord the fluxes of iron and manganese were computed to be 469 μg Fe cm^{-2} yr^{-1} and 15.6 μg Mn cm^{-2} yr^{-1} respectively.

These latter fluxes represent upper limits, as probably not all manganese and iron would be precipitated within the inner fjord basin. The above fluxes combined with the concentration of copper on particles (0.32 μg mg^{-1}), yields fluxes of copper to the sediment by particulate iron and manganese material of 0.15 ± 0.06 μg Cu cm^{-2} yr^{-1} and 5 ± 2.4 X 10^{-3} μg Cu cm^{-2} yr^{-1} respectively. These fluxes of copper by the above particle types are two to four orders of magnitude less than the estimated removal rate from the water column (16.5 μg Cu cm^{-2} yr^{-1}). Considering these data and the elemental ratios in Gulf of Alaska and Resurrection Bay sediments (Table 16) it appears that neither iron nor manganese particles are alone responsible for the transport of copper to the sediments of Resurrection Bay.

All the preceeding calculations of potential copper fluxes to the sediment are summarized in Table 17. The agreement between undifferentiated particle flux and the measured rates of loss from the water column reinforces the observation that suspended particles are responsible for the transport to the sediment surface. The marked disagreements between the measured copper fluxes and copper fluxes due to clays and silts and particles of manganese and probably also of iron indicate that these particles alone cannot be responsible for the flux of copper from the water column to the sediment.

Recent analysis of particulate matter from the northeast Gulf of Alaska (Feely *et al.*, 1976) show that copper is enriched in organic

TABLE 17

Comparison of Potential Copper Fluxes to the Sediment *via* Biogenic, Clay and Silt Sized, Iron and Manganese Particles with Measured Fluxes

Method of Calculation	Flux μg Cu cm^{-2} yr^{-1}
Measured net rate of copper loss from the water column	
Assumed to particulate matter, hence to sediment. Integrated deep water removal flux (Table 15).	Range : 9.9 to 2.6 Mean : 5.5
Estimated mean net integrated removal from total water column.	16.5
Undifferentiated particle flux	
Calculated from; average particulate matter concentration, concentration of Cu on particles (0.32 μg mg^{-1}) and settling velocities for particle sizes between 1.4 and 50 μm.	0.4 to 55
Biogenic particle flux	
Biogenic particle flux through the water column controlled by primary productivity in surface waters. Carbon flux to the sediment converted to copper flux by utilization of Cu:C ratio in phytoplankton.	Range : 13.7 to 38.5
Clay and silt sized particle fluxes	
Clay and silt sized particle fluxes into Resurrection Bay (calculated from sediment discharge rate and size distributions of sediment in runoff, U.S. G.S. data) were combined with the concentration of copper on particles (0.32 μg Cu mg^{-1}).	
Clay size	276 ± 206*
Silt size	205 ± 123*
Manganese and iron particle fluxes	
Computed from concentrations of dissolved and particulate iron and manganese in Resurrection River runoff and rates of freshwater river input (USGS) and concentration of copper on particles (0.32 μg mg^{-1}).	
Iron	0.15±0.06*
Manganese	5.0 ±2.4 x 10^{-3}*

*The statistics, standard errors, are probably insignificant with respect to the assumptions discussed in the text; standard errors reflect only variances of data used in the calculations.

matter of marine origin. Boström *et al.*, (1975) have shown, with mixing models, that up to 95% of the copper in Pacific and Atlantic pelagic sediments was derived from biological matter. A hypothesis of biogenic transport of copper to the sediments in Resurrection Bay seems well supported.

Sediments and Interstitial Waters

The Fjord Sink for Copper

The foregoing discussion has demonstrated that:

(i) copper is lost from the water column onto suspended particulate matter and transported to the sediments, and

(ii) copper is remobilized from the solid phase(s) in the surface sediments and refluxed into the overlying water.

Each of the above processes dominated the deep water copper budget at different times of the year. Net losses dominated between June and January (summer-mid winter) but net increases dominated between February and May (winter-spring); a reflection, it is proposed, of the seasonal variations in particulate fluxes through the fjord (Fig. 17). The overall relative effects of processes contributing to a budget can be assessed if the rates at which they operate are integrated through space and time. This latter is done below to compute the proportion of copper removed from the water column and carried to the sediment which is returned to the overlying water. The following facts and assumptions are used.

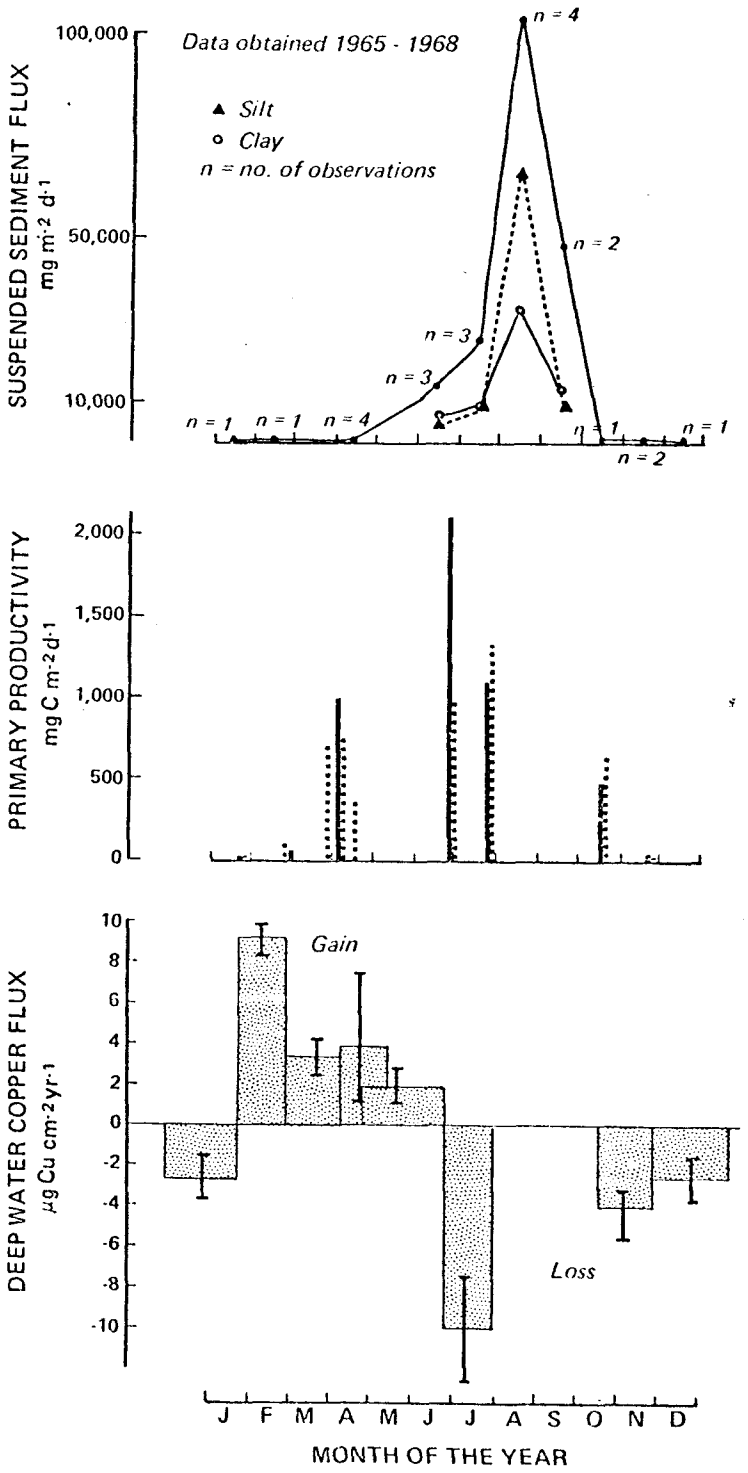


Figure 17. Seasonal variations of; deep water copper fluxes, biogenic and clay and silt sized particle fluxes through Resurrection Bay.

1. Net losses of copper from the water column were computed from the bottom 100 m of the water column between June and January at an average rate of 0.55 µg Cu ℓ^{-1} yr^{-1} (Table 15, p. 103). It is assumed that removal processes dominate over remobilization processes in the upper two hundred meters of water column at the same rate.

2. Net increases of copper were computed in the bottom 100 meters of the water column between February and June at an average rate of 0.46 µg Cu ℓ^{-1} yr^{-1} (Table 15, p. 103). It is assumed that removal processes, because of a continued but much reduced particle flux in the water column, dominates the upper 200 meters of water column between February and June at an average rate of 0.55 µg Cu ℓ^{-1} yr^{-1}. This assumption provides an upper estimate of the quantity of copper removed from the water column.

The net removal of copper from the water column over a one year period, for a 1 cm^2 surface of water column, therefore is:

$$\int_0^h \int_0^{t_1} R_1 \, dZ \cdot dt + \int_{Z_1}^h \int_{t_1}^{t_2} R_1 \, dZ \cdot dt \qquad (4.9)$$

where, R_1 = 0.55 µg Cu ℓ^{-1} yr^{-1}, h = 300 m, Z = 100 m t_1 = 7 months. This is numerically equal to 14.2 µg Cu.

The net input of copper to the water column by remobilization processes is:

$$\int_0^{Z_1} \int_{t_1}^{t_2} R_2 \, dZ \cdot dt \qquad (4.10)$$

where, R_2 = 0.46 µg Cu ℓ^{-1} yr^{-1}, Z_1 = 100 m, t_1 = 7 months, t_2 = 12 months. This is numerically equal to 1.9 µg Cu. The ratio of copper remobilized in the surface sediments and returned to the overlying water, to the total copper carried to the sediment is therefore 1.9/14.2 i.e., about 13%.

The greatest uncertainty in the above calculation is introduced by the assumption that removal processes continue during the winter period January-June throughout the top 200 m of water column at the high rates calculated from summer data. More realistically, removal processes during the winter, in the upper 200 m of water column, are either insignificant or continue at much reduced rates because of considerably lower particulate matter fluxes. Assuming that removal processes in the upper 200 m of water column during the winter are insignificant (neglecting the second term in equation 4.9) a lower estimate of copper removed from the water column was found to be 9.6 µg Cu. The ratio of copper remobilized in the surface sediments and returned to the overlying water, to the total copper carried to the sediment is, under these conditions, therefore about 20%. The sediments then are a sink for copper.

Removal in Sediments

The sediments beneath about 10 cm depth in the inner basin of Resurrection Bay are anoxic and hydrogen sulfide is produced by bacterial reduction of sulfate from seawater (Richards, 1965). The solubility of copper sulfide (pK_s = 35.2) is several orders of magnitude lower than that of iron sulfide (pK_s = 17.2) (Ringbom, 1963), which

suggests as a first approximation, subject to kinetic limitations, that copper would be more effectively precipitated as a solid sulfide than would iron. The absence of free hydrogen sulfide and the high ($\sim$20,000 mg kg^{-1}) iron concentrations in the sediments suggests that sulfides produced are precipitated as metallic sulfides. Hence, a mechanism is available, below about 10 cm depth in the sediments, to readily remove copper from solution.

Interstitial water copper concentrations show some variability, particularly at the sediment surface, but this is believed to be the result of sampling from a heterogenous surface sediment moreso than a significant time difference. Most significant is the consistent profile shape that persists over about a twelve month period. A sharp gradient directed into the sediment persists between the surface segment and the immediate segment below. The interstitial water copper concentrations below about 7-cm depth cannot be explained by simple burial of the surface segment; a removal process must be invoked. The minima observed between about 7 and 20-cm depth and the discontinuous nature of the depth distribution suggests that removal occurs principally in a narrow zone between about 7 and 20 cm; concentrations below 20 cm may be explained, at least in part, by simple burial without any further removal reaction. Concentrations below about 20-cm depth appear to increase from about 2 μg ℓ^{-1} to 3 to 4 μg ℓ^{-1} at about 120-cm depth. The gradient and apparent concentration increase may result from a secondary remobilization from the solid, probably sulfide, phases and a distillation effect (Appendix C) as interstitial waters migrate up-

ward. The gradient, if real, indicates diffusion of copper from a source deep within the sediment into the narrow removal zone focused at about 10 cm depth.

Several kinetic models of the distribution of dissolved chemical species in interstitial waters have been described. Berner (1971), for example, explained curvature in interstitial water profiles as a result of the combined effects of advection and diffusion and a reaction term that may be zero or first order in concentration. The discontinuous copper profile in Resurrection Bay sediments, however, could not be described by simple models apparently because both production and removal processes proceed, it is proposed, in relatively narrow zones. The principal removal of copper from interstitial waters appears to occur in a zone between about 7 and 20 cm depth. A removal reaction proceeding below about 20 cm depth cannot be argued for in the absence of a gradient to indicate supply of copper to deeper depths. The rate of removal of copper from Resurrection Bay interstitial waters has been computed considering supply both from above and from below the apparent removal zone. The removal rate is comprised of:

i. the diffusive flux of copper from the surface segment, plus,

ii. the rate at which the sediment surface is being buried minus the advective flux of upward flowing interstitial water due to compaction of sediments, and

iii. the diffusive flux from below the reaction zone, plus

iv. the advective flux due to sediment compaction minus the rate of sediment burial.

This may be written: (4.11)

$$-D_s \frac{\Delta C}{\Delta Z}(0/7\ \text{cm}) + (W - W_c)\Delta C_{(0/7\ \text{cm})} + D_s \frac{\Delta C}{\Delta Z}(20/120\ \text{cm}) - (W - W_c)\Delta C_{(20/120\ \text{cm})}$$

where: D_s = diffusion coefficient of copper in sediment

C = concentration of interstitial copper ($\mu g\ \ell^{-1}$)

Z = depth into sediment

W = sedimentation rate (burial)

W_c = interstitial water upward velocity

For $W \sim Wc$, (Berner, 1971) advective effects are negligible and the equation is dominated by the diffusive flux terms, (the difference $W-W_c$, needs to approach 10 cm yr^{-1} for the advective flux to be of the same order of magnitude as the diffusive terms). The rate of removal of copper is:

$$-D_s \frac{\Delta C}{\Delta Z} (0/7 \text{ cm}) + D_s \frac{\Delta C}{\Delta Z} (20/120 \text{ cm}). \qquad (4.12)$$

For a value of $D_s = 3 \times 10^{-6}$ cm^{-2} sec^{-1} (Fanning & Pilson, 1972) the flux of copper to the removal zone is 0.08 μg Cu cm^{-2} yr^{-1}, and assuming this is all removed uniformly in a thin 20 cm zone, it is equivalent to a reaction net average removal rate of 4.1 μg Cu ℓ^{-1} yr^{-1}. No account has been taken of copper transferred directly between solid phases as particles pass into the anoxic region of the sediments.

Remobilization and Flux across the Sediment-Seawater Interface

Some different mechanisms of remobilization of metals from solid phases have been described and/or discussed by e.g.'s, Bradford (1972), Brinkmann and Iverson (1975), Wood (1973), Stumm and Morgan (1970). Elucidation of the mechanism responsible for the remobilization of copper from Resurrection Bay sediments was beyond the scope of this work, but three very general possibilities are envisaged which depend,

in part, upon the particle type largely responsible for the transport of copper to the sediment; one as a direct result of biological activity in sediments and the other two principally abiotic remobilizations due to changes in the character of the chemical environment.

1. Copper carried to the sediment surface on biogenic material, and remobilized as a direct result of bacterial and heterotrophic animal activity in the surface sediments.
2. Copper carried to the sediment surface on 'inorganic particles', e.g. clays and authigenic minerals and remobilized *via* chemical chelation reactions with organic compounds in the surface sediments.
3. Copper carried to the sediment on manganese and iron oxides and hydroxides undergoing remobilization due to the chemical dissolution of these phases as a result of pE and pH changes in the sediment.

It was previously demonstrated that the persistent maximum observed in the interstitial water concentrations could only be explained by remobilization from a solid phase. The surface interstitial water concentration was maintained despite losses from it to the overlying water and deeper regions of the sediment. With a knowledge of the rates of all the apparent removal processes of copper from surface interstitial waters, the rate of remobilization, for a steady state surface segment concentration, is equivalent to the rate of removal by precipitation deeper in the sediment plus the rate at which copper is returned to the overlying water, i.e.,

$$\underset{(R)}{\text{Remobilization rate in surface sediment}} = \underset{(r_1)}{\text{Rate of removal by precipitation}} + \underset{(r_2)}{\text{Rate of return to overlying waters}} \qquad (4.13)$$

The mean net flux of copper away from sediments into the overlying water (r_2) was 4.6 μg Cu cm^{-2} yr^{-1} (Table 15) and the flux to the removal zone in sediments (r_1) was 0.08 μg Cu cm^{-2} yr^{-1} (page 127). If it is assumed

that the remobilization proceeds uniformly in a 7-cm zone, the rate of remobilization is therefore approximately 670 μg Cu ℓ^{-1} yr^{-1} and about 98% of this is due to loss to the overlying water. A previous calculation found that up to 80% (p. 124) of the copper brought to the sediment surface by falling particles was not returned to the overlying water. These results imply that, the 80% of copper brought to the sediments which is not returned to the overlying waters, also escapes remobilization from the solid phase, and is simply buried, i.e., no other pathways of copper subsequent to remobilization appear significant other than return to the overlying waters. It appears therefore that the flux of copper to the overlying water is controlled by the relative rates of the remobilization process and the net rate at which particles are being removed from the remobilization zone by sedimentation.

In light of the remobilization process found in this work, it was logical to propose that reactions of interstitial water copper in the surface sediments may act as a control on the flux to the overlying water. Because the mixed oxides of manganese and iron are known to be effective scavengers of trace metals in natural waters (Krauskopf, 1956; Jenne, 1968), are associated with copper in the sediments (Goldberg, 1954) and exist in solid concentrations about 10^6 greater than interstitial water copper concentrations, the mixed oxides of manganese and iron loomed as possible controls on the sediment-seawater exchange of remobilized copper. Iron in oxidized surface sediments has been shown to control the flux of phosphate cross the sediment-seawater interface (Hutchinson, 1957; Price and Calvert, 1973).

However, concentrations of copper on sediments in Resurrection Bay (Table 13) did not indicate any significant accumulation of copper at the sediment-surface on oxide or carbonate phases. These data support the results of the previous calculations, i.e., reactions of copper subsequent to remobilization do not significantly control the flux to the overlying water.

It is felt that the scavenging of remobilized trace metals by precipitating manganese and possibly iron oxides and hydroxides at the sediment surface is a bona-fide mechanism to propose generally as a control on the flux of remobilized metals to overlying waters. It does not however appear important in Resurrection Bay and some data, 'complexometric titrations', (Fig. 18; measurement of 'free' copper remaining in solution after successive additions to and equilibration of aliquots of copper to a filtered seawater sample at pH $\sim$ 8.3; copper concentrations measured by DPASV) indicate that copper in the very bottom waters (a result probably of remobilization processes in surface sediments) of the deep basin is associated - possibly with organic material. (The 'curve break' observed during April indicates the association of copper with complexing matter). An association of copper with organic matter may inhibit the affinity of copper for reprecipitating manganese and iron phases and therefore provide a 'gateway' through which remobilized copper may escape scavenging at the oxidized sediment surface.

These mechanisms remain purely speculative at present, but may be significant for minor metal accumulations in manganese nodules and serve to explain, in part, the relative accumulations of copper in deep sea, over continental borderland, nodules (Appendix C; Table 4).

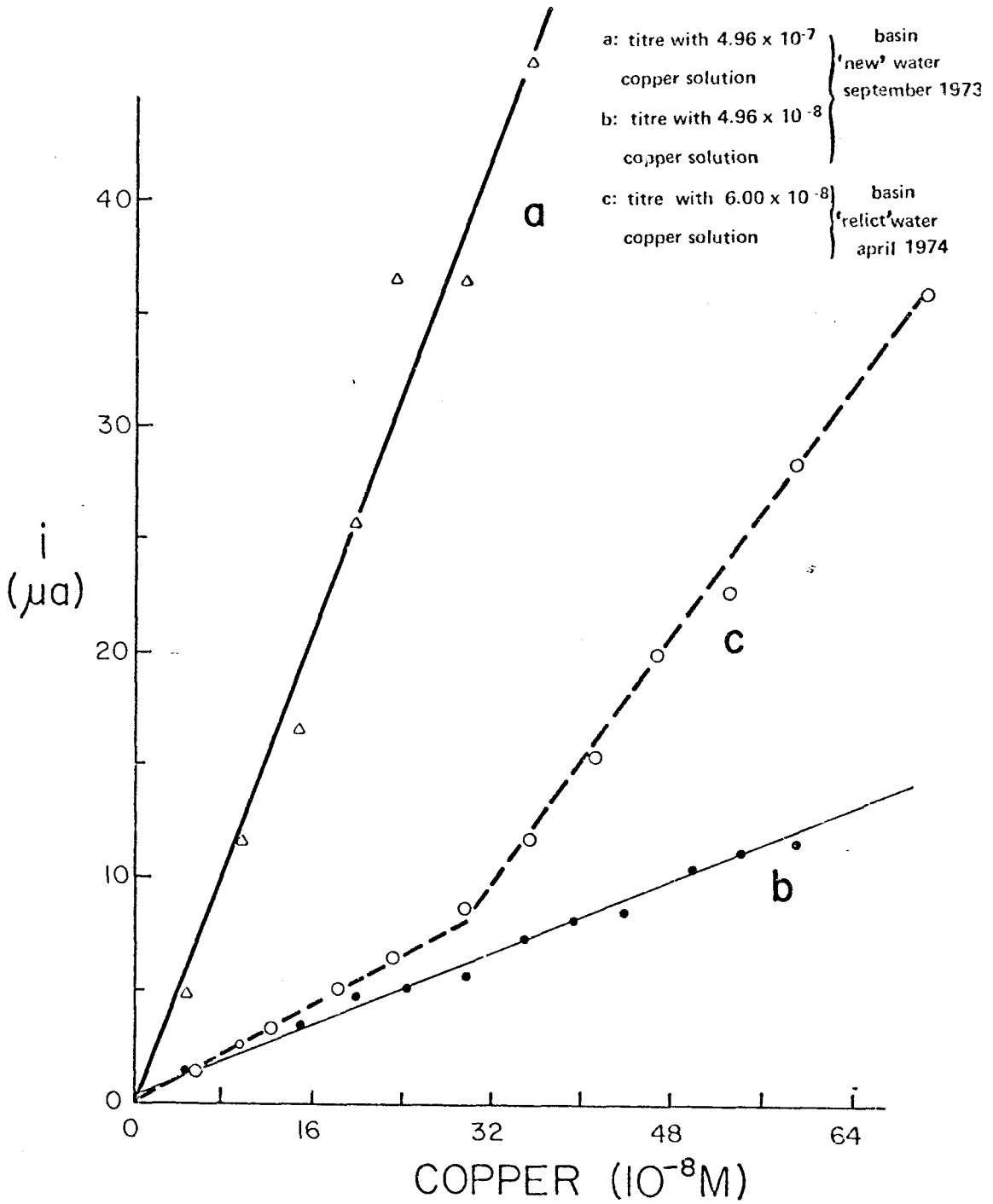


Figure 18. Complexometric titrations, with copper, of filtered seawater samples, pH ∿8.3 from the inner basin of Resurrection Bay in September 1973 and April 1974.

V. REMOVAL AND REMOBILIZATION: TENTATIVE RESULTS AND REASONING

This chapter presents reasoning and the results of some calculations which must be considered tentative only. With respect to the removal and remobilization processes found in this work this discussion is relevant.

Sediment Reaction Zones

Copper was found to be carried to the sediment surface by falling particulate material, remobilized in the surface sediments, and removed deeper within the sediments to a different solid phase; reactions in sediments appear to take place in zones. The location of the remobilization horizon, in environments of different sedimentation rates and particulate biogenic matter fluxes ought to give some information concerning the nature of the particles that are responsible for transport to the sediment surface (i.e., whether they are biogenic or inorganic). Further, the relative locations of the remobilization and removal horizons may be useful to test if the remobilization and removal reactions are confined to narrow zones in the sediments, or smeared over extended sediment depths.

In a sedimenting column, the chemical environment, as a result principally of the oxidation of organic matter, changes with depth and the oxidation intensity (pE) decreases with depth. Within this redox gradient there is a reaction sequence for many elements (Stumm and Morgan, 1970; Breck, 1975) which is in part, schematically illus-

trated in Figure 19. In deep oceanic environments, where sedimentation rates and organic loads are both relatively low, the gradient in redox intensity generally would be expected to be slight and oxidation-reduction reactions of the types shown in Figure 19b, are probably separated by relatively large vertical distances. This is to be contrasted to continental borderland and estuarine sediments having relatively high sedimentation rates and organic loads; the redox intensity gradient would be greater with the same reaction sequence compressed into a relatively thin surface-sediment layer. These controls on a redox gradient by sedimentation rate and organic load are illustrated in Figures 19a and 19c.

Because of the widespread associations of manganese and copper in the sea, interstitial water manganese profiles in environments of different sedimentation rates are illustrated with respect to the above (Figs. 19a and 19c). Deep sea oceanic sediments are generally oxidizing (Lynn and Bonatti, 1965) and manganese oxide phases are stable to relatively great depths, but at continental borderlands where hydrogen sulfide may be found at shallow depths, manganese oxides are unstable and reduced to Mn (11) in near surface sediments. Sediment and interstitial water profiles of manganese in these types of environments have been discussed by Calvert and Price (1972). The latter authors found maximum interstitial water manganese profiles in the very surface sediments of a scottish loch, but Li *et al.* (1969) found maximum interstitial water manganese concentrations at about 130 cm depth in the Arctic Ocean. Copper in the sea may be associated with mixed oxide

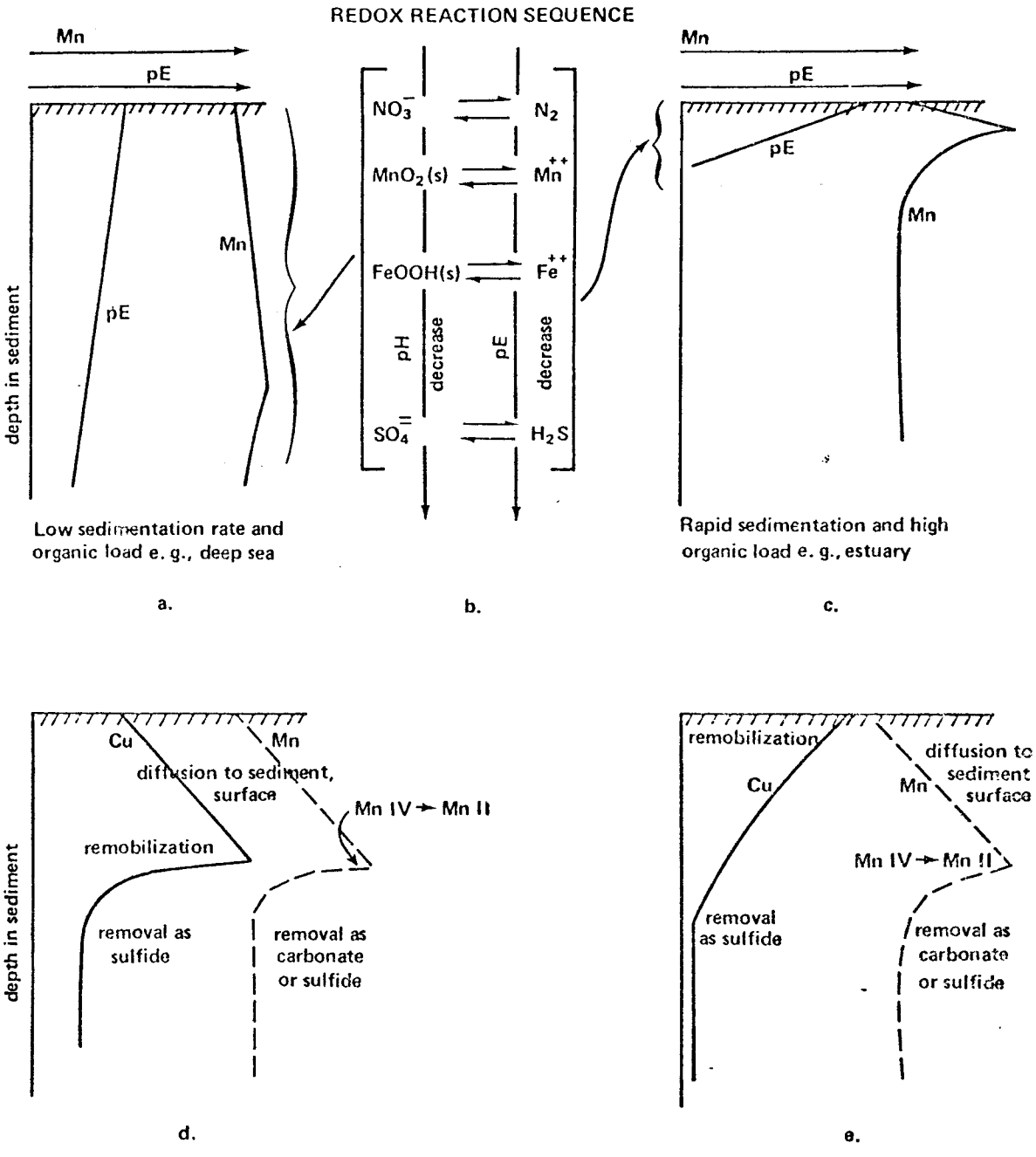


Figure 19. Schematic representation of redox intensity and interstitial water, copper and manganese profiles from environments of rapid and slow sedimentation rates.

phases of manganese and iron e.g. Goldberg (1954) and/or biogenic particulate matter e.g. Martin (1970), Lowman *et al.* (1971). Within the context of sediment redox reactions at different pE levels, the remobilization and removal reactions reported in this work, depending on the nature of the particles carrying the copper to the sediment, should occur at depths which are functions of the sedimentation rate and organic load.

Hence, the remobilization of copper that is associated predominately with particulate iron and manganese oxides would be expected to closely follow the remobilization of manganese with removal as copper sulfides proceeding deeper in the sediment under more reducing (lower pE) conditions (Fig. 19d). However, copper associated principally with oxidizable biogenic matter, would undergo remobilization in the zone (Fig. 19e) where the activities and numbers of bacteria oxidizing organic matter are at a maximum, and this is the surface sediments (Kriss, 1963). The remobilization of copper, if it were associated with siliceous tests (Kastner, 1976) would also be expected within the surface sediments where the tests dissolve in response to removal of the protective organic coating by aerobic bacterial and heterotrophic animal activity. Removal as copper sulfide would still however proceed deeper within the sediment beyond the redox discontinuity in the anoxic region. Where sedimentation rates and the particulate biogenic flux are relatively high, profiles of the types illustrated by Figures 19d and 19e, because of their compression into the surface sediment, would be indistinguishable; this appears to be the case in

Resurrection Bay. Conversely, where sedimentation rates and biogenic loads are relatively lower, these profiles may be expected to be elongated with the remobilization and removal zones physically separated in the sediments.

The above are simplistic developments based upon the supposition that copper is predominately associated with a single particle type. Because suspended particulate matter falling to the sediment surface is probably a mixture of biogenic and inorganic matter and both may be transporting copper, actual interstitial water copper profiles cannot be viewed so simplistically. Additionally, the biological reduction of copper carrying Mn IV, and Fe III surfaces (as distinct from the chemical dissolution of these phases), with subsequent release of adsorbed trace metals (Ehrlich, 1972) could confound the interpretation of interstitial water profiles.

The above reasoning, however, provides some framework to view copper profiles in interstitial waters. The location and nature of the remobilization and removal processes in sediments may be clarified, across a spectrum of environments of different sedimentation rates and organic loads with depth distributions of interstitial water, copper, manganese, iron and sulfate concentrations and the numbers, physiological types and indicators of bacterial activity in sediments. Application of models of the types described by Berner (1971) to these latter type environments should provide a useful test for zonation of reactions. If remobilization and removal reactions do occur in narrow zones, then between these end-members, the profiles in the intervening sediments should closely fit an advection-diffusion profile with no reaction

terms involved.

Tentative Copper Mass Balance: River Supply Versus Water Column Removal

If the total amount of copper introduced into the fjord during any given period, and the net removal rate of copper from the water column are known the fraction of total introduced copper that escapes removal to the sediments and is exported to the continental shelves can be computed.

There are no data available specifically for the total copper content of Resurrection River runoff. However, Durum and Haffty (1963) have assembled the median values of many minor element contents of North American rivers; the median value for copper was 5.3 μg ℓ^{-1} and this has been assumed representative of summer runoff from the Resurrection River. The mean summer (June through September) freshwater runoff into Resurrection Bay is approximately 110 m^3 sec^{-1} (USGS unpublished data). These data permit some assessment of the total copper input to the fjord between June and September and this was computed to be 6.1 ± 2.4 X 10^{12} μg Cu. (The statistic includes variances associated with river runoff and the median copper concentration in runoff.)

The net integrated removal flux from the bottom 100 m of water column was calculated to be 5.5 μg Cu cm^{-2} yr^{-1} (Table 15; p. 103) and for the total water column depth estimated to be 16.5 μg Cu cm^{-2} yr^{-1}. This removal flux dominated the water column for about 7 months of the year. Assuming this flux to be representative of the surface area of the

inner fjord basin enclosed by the sill depth contour ($\sim 5 \times 10^7$ m^2) the amount of copper removed from the water column in a year was calculated to be 4.8×10^{12} µg, i.e., $\frac{4.8 \times 10^{12}}{6.1 \times 10^{12}}$ or about 80% of copper introduced into the fjord by Resurrection River runoff is removed to the sediments of the inner basin in the area enclosed by the sill depth contour.

Although a large uncertainty is introduced into these calculations by not having available specifically the total copper contents of the Resurrection River runoff, the analysis does indicate that the relatively small area of the inner fjord is a significant trap for continentally introduced copper.

Scavenging Fluxes in the Deep Sea and Resurrection Bay: A Comparison

Craig (1974) utilized a one-dimensional advection-diffusion model to examine non-conservative behavior and compute fluxes of copper at the GEOSECS intercalibration station in the North Pacific. Craig found that between 1 and 4 km depth the observed copper profile could only be fitted to the mixing model when *in situ* scavenging of copper was invoked; the magnitude of the scavenging term was directly proportional to the average copper concentration in the deep water, 2 µg Kg^{-1}, and was found to be 1.43×10^{-3} µg kg^{-1} yr^{-1}. Recent measurements of copper in the North Pacific Ocean (Boyle and Edmond, 1975b) over the East Pacific Rise (21°N, 109°W) not far removed from the GEOSECS station (28°28'N, 121°38'W), show copper concentrations between 1 and 3 km depth of between 2 and 6 n.mole kg^{-1} or about 0.13 to 0.38 µg kg^{-1}; values which are about one order of magnitude lower

than those given by Spencer *et al.* (1970) and used by Craig (1974). Because of scatter in their data and the observation that filtered samples were higher than unfiltered samples, Boyle and Edmond (1975b) suspected that even these latter concentrations were high. If this is in fact so, then the scavenging fluxes given by Craig (1974) should be reduced about one order of magnitude, i.e., 1.43×10^{-4} µg kg^{-1} yr^{-1}.

Fluxes of trace metals to the sediment by sinking material are functions of the affinity of the particular metal for the sinking phase and the sedimentation rate. Sedimentation rates in the deep sea (approximately cm's per 1000 years) are about 3 orders of magnitude less than sedimentation rates in coastal environments. If the kinetics of adsorption for any given metal are rapid with respect to sedimentation rates then scavenging and transport to the sediment ought to be about proportional to sedimentation rates. The deep water scavenging flux from Resurrection Bay (0.55 µg Cu ℓ^{-1} yr^{-1}) exceeds that from the deep North Pacific Ocean (1.43×10^{-4} µg Cu kg^{-1} yr^{-1}) by a factor of about 4000: a factor which is of about the same proportionality as sedimentation rates in coastal environments and the deep sea. The result indicates that there is at least no order of magnitude differences in affinities of copper for the particles in the deep sea and this estuarine environment.

Craig argued that if copper is scavenged from the deep sea as well as the surface ocean, some process must be operating to maintain the maximum copper concentration in the deep water, and proposed either an inflow of Antarctic bottom water with a copper concentration of about 3

$\mu g\ kg^{-1}$ or a flux of copper across the sediment-seawater interface. The remobilization of copper in surface sediments and flux to the overlying water, undemonstrated prior to this work, may be operating in the deep sea and serve to explain Craig's (1974) observation.

VI. SUMMARY

The aims of this work were to investigate from mass balances the non-conservative behavior of copper in a fjord basin, to elucidate reservoirs as sources or sinks, to compute fluxes and to evaluate possible pathways for transports between sources and sinks. The outcome depended upon the successful integration of two distinct pieces of work:

1. The ability to make sensitive and precise measurements of copper in seawater and interstitial waters.

2. A knowledge of the seasonal variations in the nature of the exchange of water in the fjord with adjacent coastal water. The findings of each of the above are summarized below.

Copper Analyses in Sea and Interstitial Waters

1. Copper was measured in sea and interstitial waters by differential pulsed anodic stripping voltammetry using rotating glassy carbon electrodes. These electrodes had much longer useful lifetimes than wax impregnated graphite electrodes and could be used almost continuously for several months without repolishing of the electrode surface. The sensitivity with thin film electrodes was increased about five-fold over linear d.c. scan anodic stripping methods, and at the increased sensitivity level precision could be maintained at 10%.

2. Interference in copper determinations by apparent intermetallic compound formation with silver was found to be less than 1%. Analyses

were not interfered with in filtered 0.4 μm acidified (pH∿2.0) seawater by Triton-X 100, a representative surface active compound. The determination of copper in interstitial waters squeezed from the anoxic region of sediments was interferred with, possibly by electroactive polymeric type compounds; the interference was removed by oxidizing the samples in dilute nitric acid with ultra-violet radiation.

The determination of lead in seawater samples was however interfered with possibly by electroactive compounds. The interference appeared to be specific for lead and was not related to a general deterioration of the electrode surface as the electrode could be used for some time with no apparent ill effects on copper peak currents.

Exchange of Deep Water Between Resurrection Bay and the Gulf of Alaska

1. The exchange of the deep water of the inner basin of Resurrection Bay with the Gulf of Alaska follows a regular seasonal pattern. The principal exchange, advective in character, occurs during the summer and fall months, from about June through October. Gravitational displacement of the inner fjord bottom waters occurs as a result of the advection of more dense water up onto the adjacent continental shelf which subsequently penetrates the inner reaches of the fjord where it sinks to displace the resident basin water upward. The exchange appears to begin as a series of discrete influxes during May or June, but by September inflow is almost continuous. The latter appears to be controlled by the horizontal pressure gradient between the inner and outer reaches of the fjord which increases through the summer months as the more dense water advected onto the continental shelf becomes more

prominent in the outer fjord reaches. Variations in the gradient, hence of flow into the basin are probably controlled by the relative set-up of water at the coastline which changes in response to the wind field over the outer fjord and adjacent coastline. Inflow is enhanced when surface water at the coastline moves offshore but decreased when surface water is piled up at the coastline. The latter condition depresses isopycnal surfaces in the outer reaches of the fjord; hence the horizontal pressure gradient across the sill is reduced.

2. The re-establishment of a coastal convergence (October-November) and a downwelling condition at the coastline drives the more dense water down and out of the outer reaches of Resurrection Bay. The more dense summer water which remains trapped behind the sill of the inner basin exchanges predominately *via* vertical eddy mixing processes across the sill depth region with the less dense waters above sill depth during the succeeding winter. A decrease in the density of the basin water through the winter months facilitates advective exchange the following summer.

3. The intensities of vertical mixing processes just below the sill were characterized by coefficients of eddy conductivity and diffusivity and these latter varied between 1.2 and 7.3 $cm^2\ sec^{-1}$. Advective influxes into the deep inner basin had associated with them vertical velocities of the order of 10^{-2} to 10^{-3} $cm\ sec^{-1}$. During a thirty five day period in September and October of 1973, a volume of water sufficient to replace the topographic volume of the inner basin, below sill depth, four to five times over was advected through the fjord.

Integration of Physical-Chemical Data

The ocean is in constant motion. Measurements of any component dissolved in seawater are comprised of contributions from exchanges across external boundaries, reactions within the water column and advection and diffusion into and out of the region of measurement. The seasonal variations and quantitative characteristics of the exchange of water through the deep basin of Resurrection Bay were combined with measurements of copper in the water column of the fjord. Coefficients of mixing were used with copper concentration-gradients to evaluate diffusional copper exchange and, volumes of water and the concentrations of copper in effluxed and influxed basin water were used to calculate advective exchange of copper. The contributions of these latter to measured copper concentration changes in the inner basin of the fjord were evaluated and the results of these calculations were interpreted with respect to concentration changes and gradients of copper in the inner basin water column and underlying sediments. The conclusions of this work are summarized below and schematically represented in Figure 20.

Sources and Sinks, Fluxes and Pathways of Copper Through Resurrection Bay

1. Copper concentrations in filtered and acidified seawater samples ranged between 0.14 μg ℓ^{-1} and 3.13 μg ℓ^{-1}; the mean was 0.48 μg ℓ^{-1}. Concentrations of copper in sediment pore fluids varied between 1.02 μg ℓ^{-1} and 9.98 μg ℓ^{-1}. From several cores maximum interstitial water copper concentrations were always found in the surface ∿7 cm of

sediments. The mean surface segment concentration ∿8 μg ℓ^{-1} was about one to two orders of magnitude greater than concentrations in the water column. Concentrations of copper on sediments were about 20 mg kg^{-1}; three to four orders of magnitude higher than interstitial water concentrations.

2. Copper is removed from the water column (by an undefined mechanism) and transported to the sediments on particulate matter settling through the water column.

3. Copper is remobilized in the surface sediments from the solid phase(s) and returned to the overlying fjord bottom waters.

4. The mean net removal rate of copper from the water column to the sediments was 0.55 μg Cu ℓ^{-1} yr^{-1}, and was highest during the summer months (0.99 μg Cu ℓ^{-1} yr^{-1}) when particulate matter inputs to the fjord were highest. Removal reactions dominated the deep water copper budget for about seven months of the year.

5. The mean net return rate of copper from the sediments into the overlying bottom 100m of water column was 0.46 μg Cu ℓ^{-1} yr^{-1}. The remobilization of copper from the solid phase(s) is able to proceed year round as long as the particulate source of copper is not exhausted in the sediments. However, the effects of remobilization and return to the overlying waters only dominate the deep water copper budget during the winter and spring months (February through May) when particulate matter inputs to the fjord (hence scavenging removals) are minimal.

6. Between 13 and 20% of total copper removed from the water column and carried to the sediments is returned to the overlying water.

7. Copper is removed from interstitial waters, at least initially, probably by precipitation as copper sulfide. The concentrations in interstitial waters however were far in excess of equilibrium copper sulfide concentrations, and the enhanced solubility may result from subsequent reactions of the sulfide phase with organic matter in the sediments.

8. The remobilization and removal reactions in sediments are confined to narrow zones. Remobilization occurs in a zone <10 cm deep adjacent to the sediment-seawater interface. Removal appears to occur principally in a zone about 13 cm deep, adjacent to but below the remobilization horizon.

9. Effective rates of reactions in sediments may be orders of magnitude greater than reaction rates in the water column.

Future Work

It was not possible to determine unequivocally what reaction and with what particle phase copper was removed from the water column. However a comparison of the observed removal flux of copper from the water column and flux to the sediment with the potential copper flux on various particle types suggested that *in situ* biogenically derived particles only could account for the observed removal flux. The fluxes of copper on clay and silt sized particles were about fifteen times greater than the estimated removal flux and, fluxes of copper on iron and manganese particles were two to four orders of magnitude less than the estimated removal flux. The elucidation of what particle type is predominately responsible for the scavenging from seawater might be

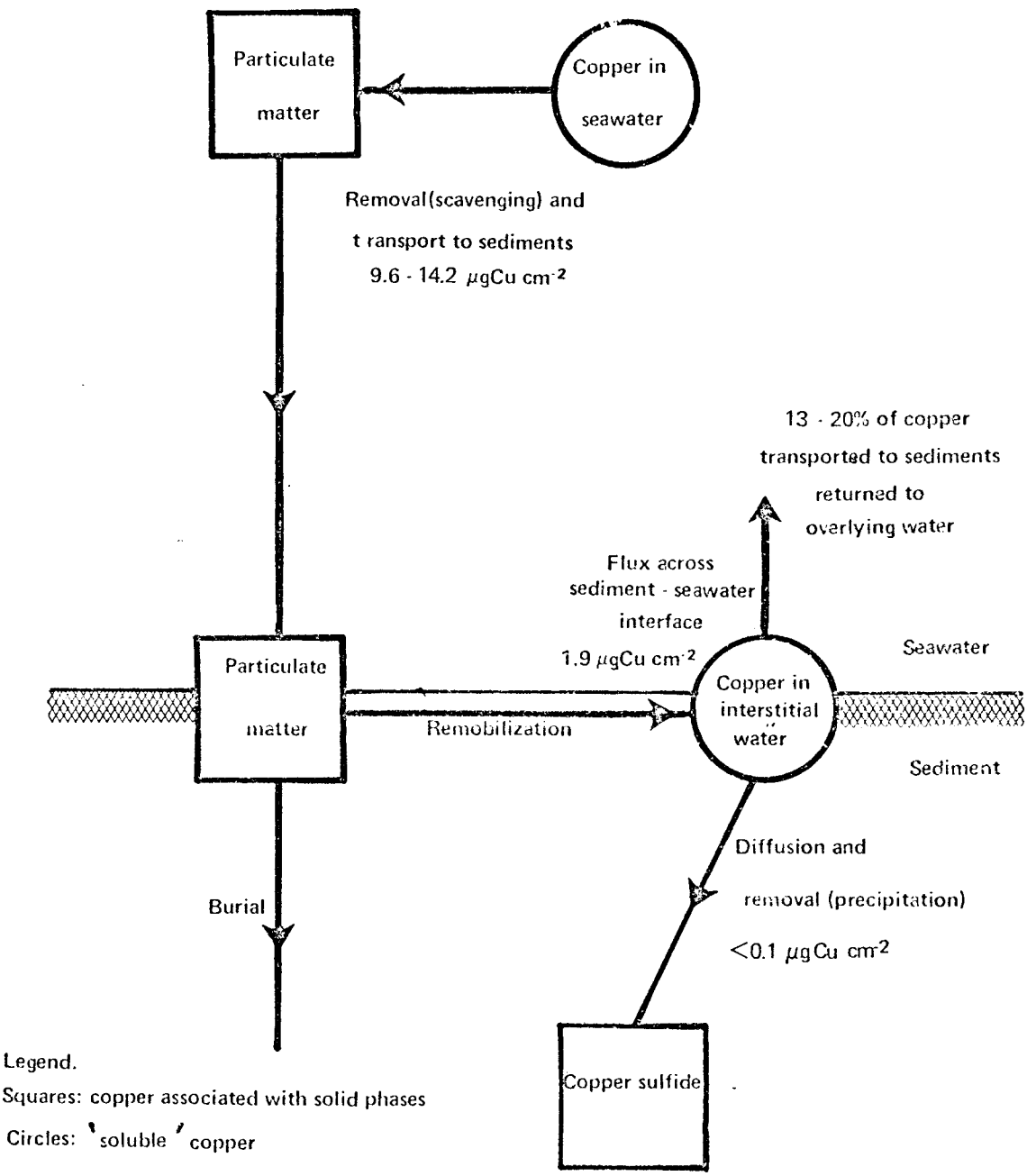


Figure 20. Schematic representation of sources, sinks, pathways and net annual transports of copper in Resurrection Bay.

evaluated in the following way. Particulate matter collected from the water column could be subjected to analysis by a technique that combined scanning electron microscopy (SEM) with energy dispersive x-ray fluorescence (EDXRF). With SEM, and statistical techniques, the relative abundances of different particle types, e.g., biogenic versus clay versus precipitating elemental oxides and hydroxides could be computed. The ability to focus on a single particle type with SEM and to obtain, by EDXRF, the relative abundances of trace metals, specifically copper, associated with each particle type would permit the relative importances of each particle type in transporting copper to be ascertained. The approach may be limited however by the sensitivity of the EDXRF; small differences in abundances of copper between particle types may need to be resolved.

Circumstantial evidence, transport of copper to the sediment by falling biogenic material and an apparent coincident 'remobilization' of copper and 'remineralization' of nutrients (N, P, Si) in the surface sediments infers that the 'remobilization' of copper is directly linked to the degradation of particulate biogenic matter. The remobilization of copper due to abiotic chemical phenomena such as solubilization of iron and manganese particles and chelation reactions in the sediments of Resurrection Bay cannot, however, be excluded. Further direction toward elucidation of the remobilization mechanism may be gained by measuring depth distributions of interstitial water copper concentrations across a spectrum of environments of different sedimentation rates and organic loads; maximum copper concentrations ought to be always found

in surface interstitial waters if the remobilization is associated principally with the degradation of organic material. The relationships between particle types and biological activity (animal and microbial) in sediments needs to be examined with respect to remobilization mechanisms of copper and other trace metals.

As long as particulate copper is supplied to the sediments the remobilization process is capable of operating continuously and, while copper concentrations in surface interstitial waters are higher than in the overlying water, a flux of copper from the sediments into the water column can be maintained. The extent of this latter however may be controlled by scavenging reactions of particles with remobilized copper in the very surface sediments as the copper passes through the redox discontinuity. This scavenging in turn may be regulated in part by the chemical form of the remobilized copper. Copper chelated with organic material might be less effectively scavenged than inorganic copper complex ions, therefore permitting more copper to escape to the overlying water. The relative effectiveness of scavenging as a function of copper concentration and chemical state, on different particle types ought to be examined.

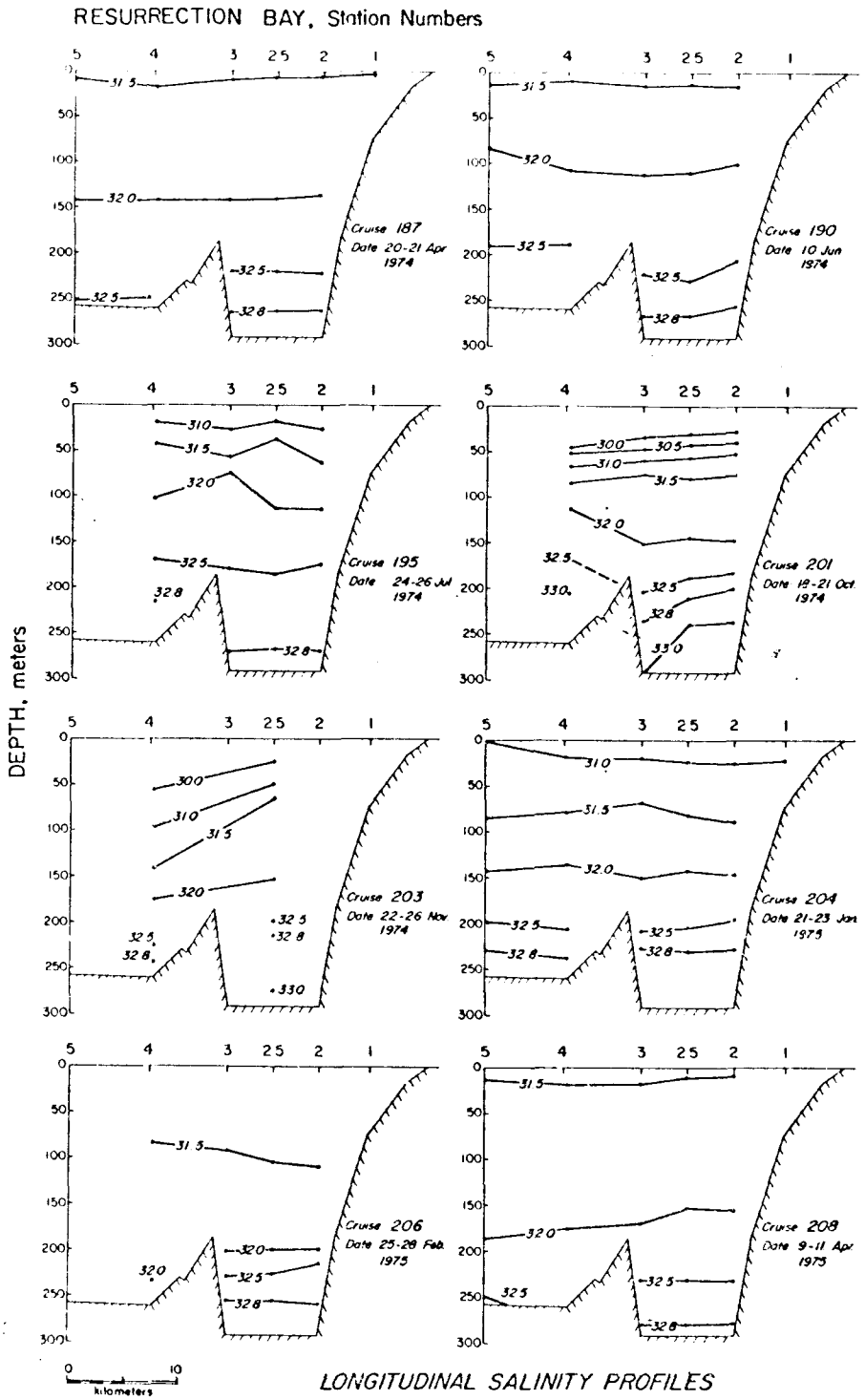
Because of the high concentrations of copper in the surface interstitial waters and the gradient in the overlying waters directed out of the sediments, it was assumed that copper in the fjord bottom waters emanated mainly from the surface sediments. It was not possible to delineate of remobilized copper in the fjord bottom waters what the relative contributions of remobilization in the water column versus

remobilization in the sediments were. This problem is common to oceanic geochemistries of other elements e.g., nutrients, nitrate, phosphate and silicate. Resolution of the above, in fjord basins, may be approached in two different ways.

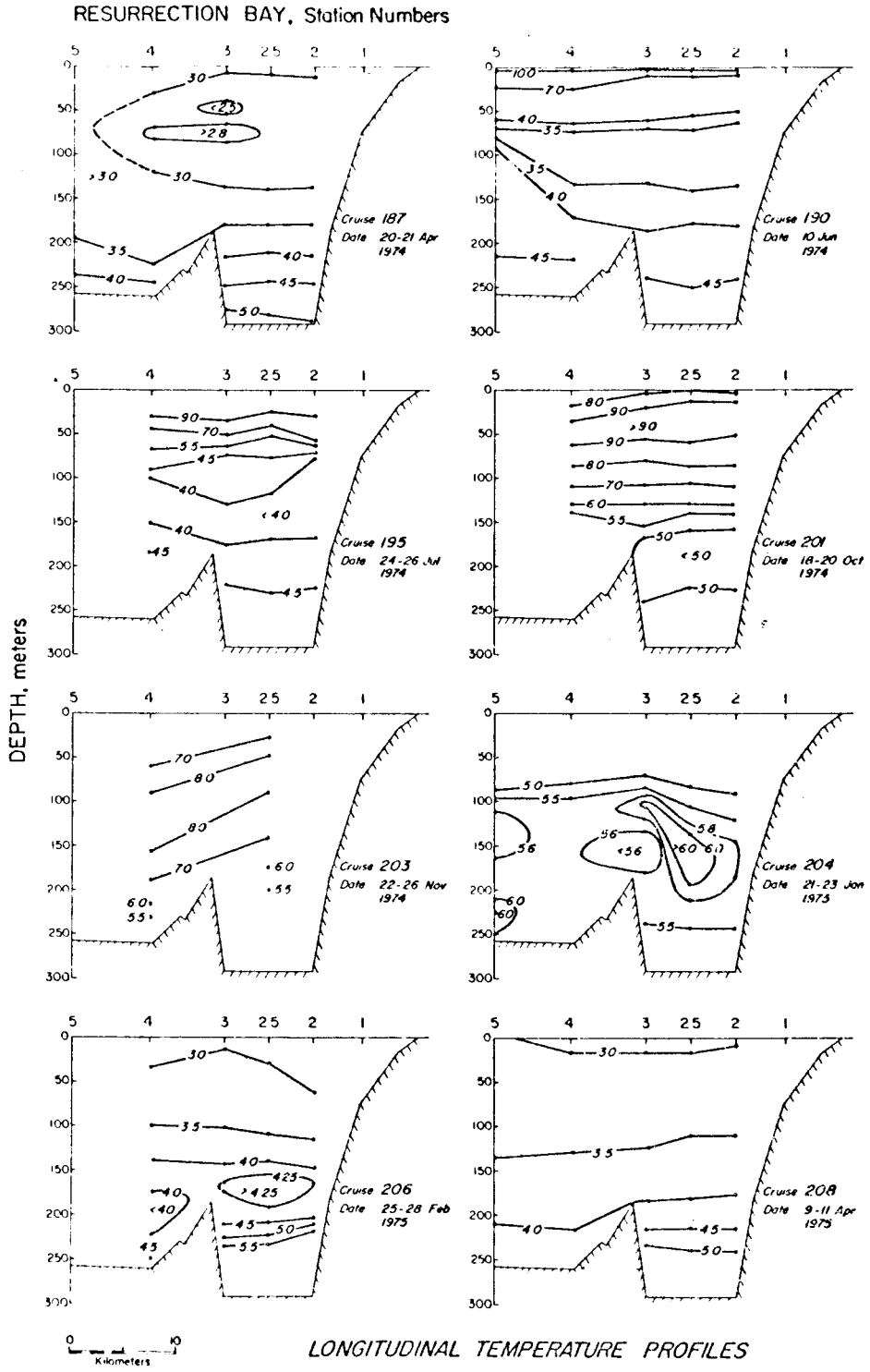
1. Vertical profiles of the species of interest may be examined with respect to fits to models describing the distribution of chemical species, assumed to diffuse from the sediments. Deviations from the predicted fit should represent contributions from reactions in the water column. The approach depends upon, but is limited by a knowledge of the vertical distribution of coefficients of eddy mixing in the seas. It appeared in Resurrection Bay that a mixing coefficient which decreased below sill depth was the best representation of the mixing processes. Measurements of radon -222, in the water column, a naturally occurring radioactive isotope which originates principally from the sediments, might prove useful in elucidating the depth distributions of mixing coefficients.

2. Stable isotope dilution techniques, applied to the bottom waters of deep fjord basins, would permit remobilization rates of copper in the water column to be determined. Between any two given time periods, a knowledge of the remobilization rate in the water column and the observed concentration change would permit the latter to be corrected for the contribution by remobilization in the water column; the remainder represents flux from the sediments. Although stable isotope techniques are available for nitrogen and silicon, a technique does not presently exist for copper.

The remobilization of copper proceeded in the surface sediments within the transition zone separating the chemical 'oxidizing' conditions in the water column and 'reducing' conditions in the sediments. Similar shaped depth-profiles, particularly a maximum in copper concentrations were found by Spencer and Brewer (1971; Fig. 4) at the redox boundary in the Black Sea. The implication is that similar processes are operating in both environments; in the Black Sea remobilization proceeds in the water column, but in Resurrection Bay, in a sedimentary column. Remobilization of metals in the ocean may be a general phenomena and elucidation of the mechanisms responsible may be found by focusing attention at redox gradients.



Appendix A - Figure 1. Fjord longitudinal salinity profiles, April 1974 through April 1975.



Appendix A - Figure 2. Fjord longitudinal temperature profiles, April 1974 through April 1975.

Vertical Mixing: Calculations of $K_{z(s)}$ and $K_{z(t)}$ (Table 6)

The general equation expressing the diffusion of salt in the vertical direction is:

$$\frac{\delta \bar{S}}{\delta t} = - \frac{\delta}{\delta Z} \left(K_Z \frac{\delta \bar{S}}{\delta Z} \right)$$

where: $\frac{\delta S}{\delta t}$ is the rate of change of salinity for any given parcel of water.

$\frac{\delta \bar{S}}{\delta Z}$ is the mean vertical salinity gradient.

K_Z is the vertical eddy diffusion coefficient.

Z is depth.

Upon integration between the depths of interest, the sill and the basin floor and, assuming no salt flux through the basin floor the equation reduces to:

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta S}{\delta t} \, dZ = -K_Z \frac{\delta \bar{S}}{\delta Z} \Bigg|_{\text{sill}}$$

The time change term has been evaluated by dividing the water column between the sill and the basin floor (ΔZ=100m) into 5 depth segments of 20 m each and rewriting this term:

$$\frac{1}{\Delta t} \sum_{i=1}^{i=5} \rho \left(S_{(t_1)} - S_{(t_2)} \right) dZ_i \qquad \text{gms cm}^{-2} \text{ sec}^{-1}$$

where: $S_{(t_1)}$ is the salinity at depth Z, at time t_1 and,

$S_{(t_2)}$ is the salinity at the same depth Z, at some later time t_2.

The term can be numerically evaluated using depth profiles of salinity. Treatment of the equation in this manner and the selection of the lower boundary condition determines K_Z at the sill only. No information about the distribution of K_Z in the basin is gained from the vertical profiles of temperature and salinity in this approach. The treatment states that the flux of matter across the upper boundary of the basin is determined by the product of a mixing coefficient and the property gradient across that boundary. The gradient in salt was obtained from the depth distributions of salinity, and the equation solved for K_Z at the sill depth. Similar comments apply to the heat budget equation, but S is replaced by the product of $C_p \times T$, where C_p is the specific heat and T is temperature. Example: From April 1973 CR: 161 to May 1973 CR:163.

A. Salt budget

Time rate of change of salt $\frac{\delta(\rho S)}{\delta t} = -1.97 \times 10^{-7}$ gm cm^{-2} sec^{-1}

Average vertical salt gradient $\frac{\delta(\rho \bar{S})}{\delta Z} = 9.0 \times 10^{-8}$ gm cm^{-4}

$$K_Z(\text{salt}) = - \frac{-1.97 \times 10^{-7} \text{ gm cm}^{-2} \text{ sec}^{-1}}{9.00 \times 10^{-8} \text{ gm cm}^{-4}}$$

$$= 2.2 \text{ cm}^2 \text{ sec}^{-1}$$

B. Heat budget

Time rate of change of heat, $\frac{\delta(\rho CpT)}{\delta t} = -4.29 \times 10^{-4}$ cal cm^{-2} sec^{-1}

Average vertical heat gradient $\frac{\delta(\rho CpT)}{\delta Z} = 1.46 \times 10^{-4}$ cal cm^{-4}

$$K_Z(\text{heat}) = - \frac{-4.29 \times 10^{-4} \text{ cal cm}^{-2} \text{ sec}^{-1}}{1.46 \times 10^{-4} \text{ cal cm}^{-4}}$$

$$= 2.9 \text{ cm}^2 \text{ sec}^{-1}$$

Vertical Mixing: Variable versus Constant Mixing Coefficients with Depth

Variations of mixing coefficients in the ocean are of interest to physical oceanographers who are concerned with distributions of, and rates of transfer of salt, heat, and momentum, but also to chemical oceanographers concerned with transports of chemical species from sources to sinks. Horizontal mixing occurs along isopycnal surfaces and coefficients are approximately three orders of magnitude greater than coefficients of vertical mixing which occurs across isopycnal surfaces; vertical mixing is suppressed by bouyancy forces. Vertical mixing coefficients, K_Z, in deep ocean mixing models e.g., (Craig, 1969) have commonly been assumed constant with depth. This assumption is not necessarily valid in estuarine environments where the temporal and spatial variations of mixing processes probably operate over smaller scales than in the deep ocean. The following analysis utilizing the observed salinity distributions in Resurrection Bay examines, but rather crudely, the apparent vertical distribution of K_Z in the deep inner fjord basin. Inspection of the time and depth distributions of salinity in Fig. 7, (p.) indicates:

a) some curvature below the sill from October through March, and

b) approximate linear distributions between March and June.

Case 1: K_Z is constant with depth between the sill and the basin floor.

$$\frac{\delta S}{\delta t} = \frac{-\delta}{\delta Z} \left(K_Z \frac{\delta S}{\delta Z}\right).$$

The equation on expansion of the term on the RHS, and assuming K_Z to be constant with depth reduces to:

$$\frac{\delta S}{\delta t} = -K_Z \left(\frac{\delta^2 S}{\delta Z^2}\right)$$

which on integration from the sill to the basin floor:

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta S}{\delta t}\, dZ \quad = \quad -K_Z \int_{\text{bottom}}^{\text{sill}} \frac{\delta^2 S}{\delta Z^2}\, dZ$$

reduces to:

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta S}{\delta t}\, dZ \quad = \quad -K_Z \left.\frac{\delta S}{\delta Z}\right|_{\text{bottom}}^{\text{sill}}$$

Assuming no salt flux through the basin floor implies either; $K_Z = 0$, or the salinity gradient, $\frac{\delta S}{\delta Z} = 0$ at the bottom. The first condition violates the original assumption of a constant K_Z with depth. The second, from inspection of vertical salinity, profiles does not appear to be valid except immediately after the advective replacement of bottom water, e.g., (September, October). All other salinity distributions indicate significant salinity gradients approaching the basin floor. In the absence of some other suitable lower boundary condition constant mixing with depth does not appear compatible with the observed salinity profiles.

Case 2: K_Z is an unspecified function of depth between the sill and the basin floor.

$$\frac{\delta S}{\delta t} = -\frac{\delta}{\delta Z}\left(K_Z \cdot \frac{\delta S}{\delta Z}\right).$$

Inspection of the time and depth distributions of salinity at Res-2.5 (Fig. 7) indicates that by about March both the time rate of change

of salinity ($\frac{\delta S}{\delta t}$) and the vertical salinity gradient ($\frac{\delta S}{\delta Z}$) approach constant functions of depth between the sill and the basin floor. The condition permits some simplification of the above equation, identical to what was done in the Santa Barbara basin (Sholkovitz and Gieskes 1971).

$$\text{i.e., } \frac{\delta S}{\delta t} = A, \text{ and } \frac{\delta S}{\delta Z} = B.$$

The above relationship holds for about four months only (March through June), and below sill depth only, at most of the sample depths (Fig. 7), to the basin floor. Substitution into the one-dimension diffusion equation:

$$A = - \frac{\delta}{\delta Z} (K_Z \, B)$$

and upon integration between the sill and the basin floor:

$$\int_{\text{bottom}}^{\text{sill}} A \, dZ = - \int_{\text{bottom}}^{\text{sill}} \frac{\delta}{\delta Z} (K_Z \, B) \, dZ$$

expansion of the term on the right hand side, simplification and assuming no salt flux across the sediment-seawater interface, i.e., K_Z=0, the above expression reduces to:

$$K_Z = - \frac{A}{B} Z \Big|^{\text{sill}}$$

Hence K_Z varies linearly with depth between the basin floor and sill depth.

Example: From May 7 CR:163 to May 22, 1973 CR:166. The average time rate of change of salinity between the sill and the basin floor is:

$$\frac{\delta S}{\delta t} = 3.7 \times 10^{-8} {}^{o}/_{oo}\ \text{sec}^{-1} = A$$

and the vertical salinity gradient over the same interval

$$\frac{\delta S}{\delta Z} = 8.00 \times 10^{-5} {}^{o}/_{oo}\ \text{cm}^{-1} = B$$

the diffusion coefficient around sill depth (200 m) is:

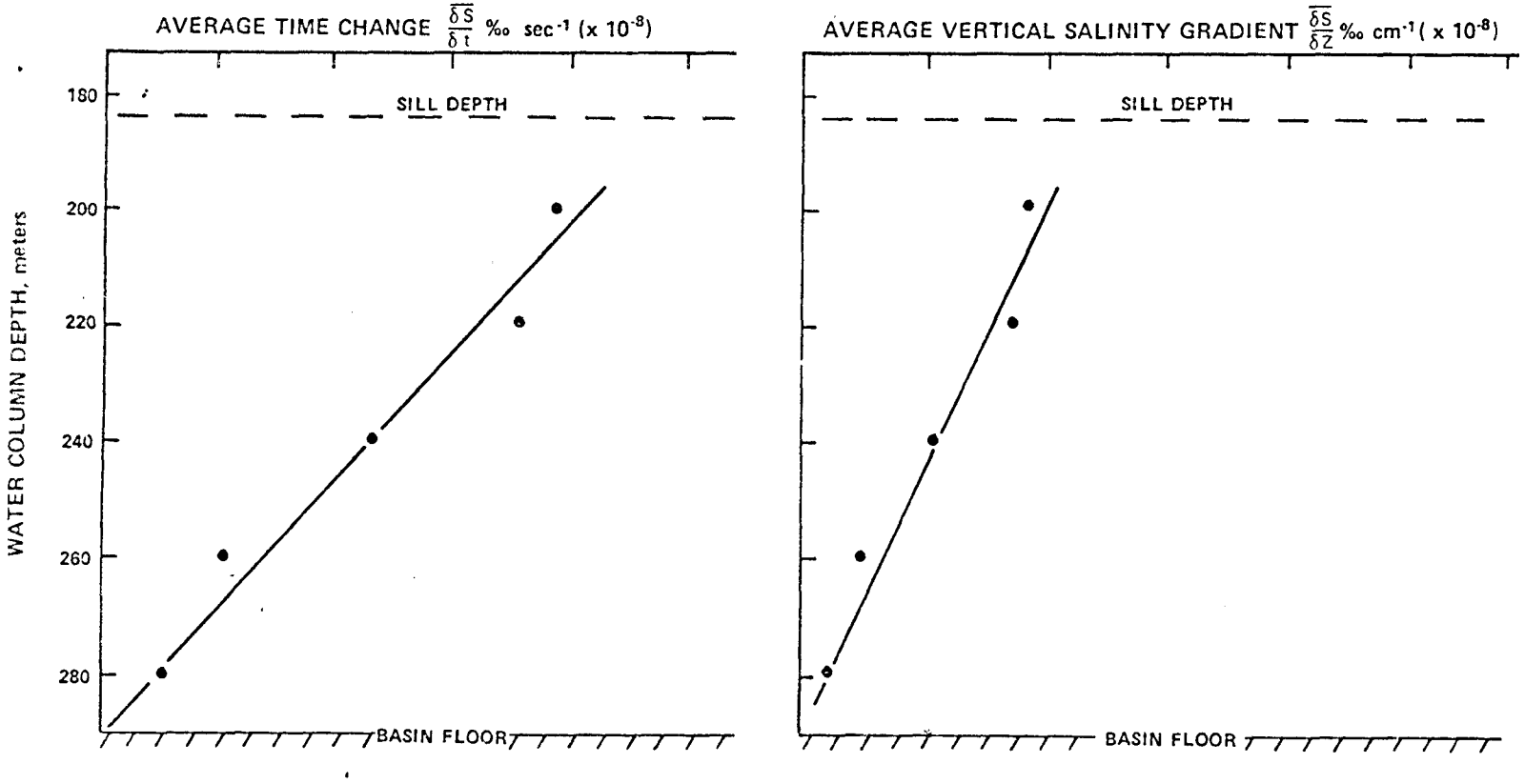
$$K_Z = \frac{-3.7 \times 10^{-8} {}^{o}/_{oo}\ \text{sec}^{-1}}{-8.0 \times 10^{-5} {}^{o}/_{oo}\ \text{cm}^{-1}} \times 9000\ (\text{cm})$$

$$= 4.2\ \text{cm}^2\ \text{sec}^{-1}$$

Case 3: K_Z is some unspecified function of depth.

$$\frac{\delta S}{\delta t} = \frac{-\delta}{\delta Z} \left(K_Z \frac{\delta S}{\delta Z}\right).$$

The distributions of salinity between about October and March show some curvature (Fig. 7). The time rate of change of salinity $(\frac{\delta S}{\delta t})$, and the vertical salinity gradients between the sill and the basin floor vary with depth. Both of $\frac{\delta S}{\delta t}$, and $\frac{\delta S}{\delta Z}$, are larger around the sill (200 m) than the corresponding terms approaching the basin floor (280 m). To illustrate, plots of $\frac{\delta S}{\delta t}$, and $\frac{\delta S}{\delta Z}$ versus depth (Z), between the sill and the basin floor are shown in figure 3 for the period October through November, 1973. The October to November 1973 data indicate that $\frac{\delta S}{\delta t}$ and $\frac{\delta S}{\delta Z}$ may be closely approximated as linear functions of depth.



Appendix A - Figure 3. Average rate of change of salinity, and the average vertical salinity gradient as functions of depth at Res-2.5, October-November 1973.

$$\text{i.e., } \frac{\delta S}{\delta t} = AZ \text{ and } \frac{\delta S}{\delta Z} = BZ,$$

A and B represent the slopes of the respective lines. Substitution into the one-dimension diffusion equation yields:

$$\int_{\text{bottom}}^{\text{sill}} AZ \, dZ = - \int_{\text{bottom}}^{\text{sill}} \frac{\delta}{\delta Z} (K_Z \cdot BZ) \, dZ.$$

which on integration becomes:

$$\frac{1}{2} AZ^2 \Big|_{\text{bottom}}^{\text{sill}} = - \; K_Z \times BZ \Big|_{\text{bottom}}^{\text{sill}}.$$

Assuming no salt flux through the bottom i.e., $K_Z = 0$, at $Z = 0$ the resulting expression yields K_Z as a linear function of depth.

$$K_Z = - \frac{A}{2B} \times Z \Big|_{\text{bottom}}^{\text{sill}}$$

Example: From October CR:180 to November 1973 CR:182

$$\frac{\delta S}{\delta t} = AZ \quad \text{and} \quad A = -5.4 \times 10^{-12} \, {}^{\circ}/_{\circ\circ} \, \text{sec}^{-1} \, \text{cm}^{-1}$$

$$\frac{\delta S}{\delta Z} = BZ \quad \text{and} \quad B = 4.6 \times 10^{-9} \, {}^{\circ}/_{\circ\circ} \, \text{cm}^{-2}$$

$$\text{i.e., } K_Z(200 \text{ m}) = - \frac{A}{2B} \times 9000$$

$$= 5.3 \text{ cm}^2 \text{ sec}^{-1}$$

The number agrees to about 20% of that derived in Table 6 (p. 47) from the salt budget. Similar plots of the time rate of change of salinity, $\frac{\delta S}{\delta t}$ and the vertical salinity gradient $\frac{\delta S}{\delta Z}$ for the period October through November 1974 indicated them to be not linear, but some higher order

functions of depth. The latter means that K_Z may be a more complex, but it may still be linear, function of depth in the basin. The foregoing treatments are based on the supposition that the vertical profiles of temperature and salinity during the periods considered were controlled by vertical mixing processes only. Curvature in the profiles may be generated by horizontal advection, and this is a real possibility especially around and immediately below the sill depth. The purpose of this effort was to demonstrate that mixing (represented by K_Z) in the basin throughout the winter months appeared to be best represented by a coefficient that decreased with depth in the deep basin.

Vertical Advection with Diffusion: Calculations of Vertical Advection Velocities and Volumes of Water Exchanged Due to Influxes to the Deep Basin (Table 7 and 8)

Salt and heat budgets, have been used to compute the volumes of water and the vertical velocities associated with advective exchange through the deep basin behind the sill.

Method 1:

The contribution to the salt budget is expressed as the product of a transport (volume/time) and the difference between the average salinities of the incoming ($\bar{S}_I$) and effluxed ($\bar{S}_E$) water. For a water column 1 m^2 in cross-sectional area.

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta S}{\delta t}\, dZ = (\bar{S}_I - \bar{S}_E)\, \frac{1}{\Delta t} \int_{o}^{h} dZ - K_Z \int_{\text{bottom}}^{\text{sill}} \frac{\delta^2 S}{\delta Z^2}\, dZ.$$

where: $\frac{\delta S}{\delta t}$ is the time rate of change of salinity at any given depth Z

K_Z is the vertical eddy diffusion coefficient

$\frac{\delta S}{\delta Z}$ is the vertical salinity gradient

$\bar{S}_I$ is the average salinity of the water influxed into the basin

$\bar{S}_E$ is the average salinity of the water effluxed from the basin.

The integral $\int_o^h dZ$ is the height h of a water column and (h x 1 m^2 cross-sectional area) is the volume of water, adding salt at the rate $(\bar{S}_I - \bar{S}_E)/\Delta t$, required to account for the computed change in salt content of the basin. The h is not necessarily the same as the distance between the sill and Z* (depth of penetration of the influx): the latter is an indicator only of the advective process.

The time rate of change of salinity is evaluated from:

$$\frac{1}{\Delta t} \sum_{i=1}^{i=5} \rho \, (S_{t_1} - S_{t_2}) \, dZ_i \text{ gms cm}^{-2} \text{ sec}^{-1}$$

where, Δt is the total time period between observations and

S_t is the salinity at any given depth between the sill and the bottom. The subscripts 1 and 2, indicate periods of observations; S_{t_2} being the salinity at any given depth measured some time after the measurement of St_i. The water column between the sill and basin floor was divided into 5 depth segments of 20 m each to compute this term. Each S is assumed to represent the mean salinity of each 20 m depth interval.

The advective contribution depends upon a knowledge of both $\bar{S}_I$ and $\bar{S}_E$. The depth to which the influx of more dense water penetrated (Z*)

can be approximated as the depth at which there is no change in density observed at time t_2, (σ_t*). S_I can then be found from the depth distribution of salinity at the station beyond the sill (Res-4) at σ_t*. $\bar{S}_E$ is approximated by the average salinity at time t_1, between Z* and the sill.

The diffusional loss of salt from the basin, reduces to:

$$K_Z \times \frac{\delta S}{\delta Z} \text{ (sill)},$$

if it is assumed there is no salt flux across the basin floor. K_Z is the vertical diffusion coefficient, and $\frac{\delta S}{\delta Z}$ (sill) is the average salinity gradient across the sill. Similar comments apply to the heat budget equation:

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta(C_p T)}{\delta t}\, dZ = C_p(\bar{T}_I - \bar{T}_E)\frac{1}{\Delta t}\int_{o}^{h} dZ - K_Z \int_{\text{bottom}}^{\text{sill}} \frac{\delta^2(CpT)}{\delta Z^2}\, dZ.$$

Example: From May CR:166 to July CR:171 1973. The distributions of temperature and salinity are shown in Figure 4. The cross hatched areas represent the salt and heat changes in the water column as a result of the advective influx. The depth of penetration of the incoming water Z* = 255 m.

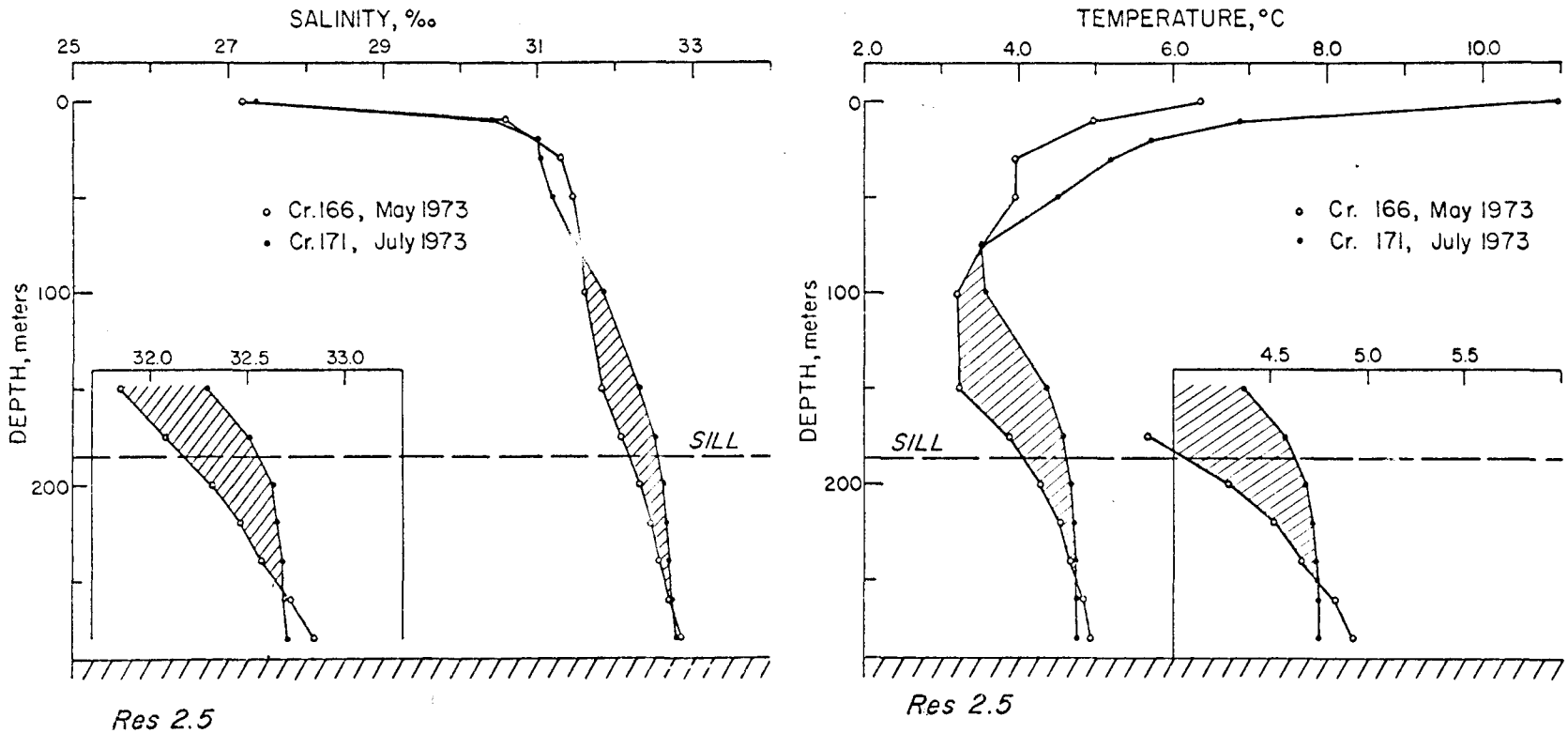
Density of incoming water (σ_t = 25.91).

From the distribution of salinity and temperature at Res-4, July 1973

$$S_I = 32.69°/_{oo}$$

$$T_I = 4.76°C.$$

From the distribution of salinity and temperature at Res-2.5, May 1973



Appendix A - Figure 4. Vertical profiles of temperature and salinity Res-2.5, May and July 1973. Cross-hatched area indicates affects of advective process on temperature and salinity.

$$S_E = 32.46°/_{oo}$$

$$T_E = 4.49°C$$

and: $\Delta t = 45.2$ days

$$K_Z = 3.00 \text{ cm}^2 \text{ sec}^{-1}.$$

Salt gradients across the sill:

$$\frac{\delta S}{\delta Z} \text{ (sill) May} \sim 8.0 \times 10^{-8} \text{ gm cm}^{-4}$$

$$\frac{\delta S}{\delta Z} \text{ (sill) July 6} \sim 1.7 \times 10^{-8} \text{ gm cm}^{-4}$$

Average salt gradient $\sim 4.8 \times 10^{-8}$ gm cm^{-4}.

Temperature gradients across the sill:

$$\frac{\delta(T)}{\delta Z} \text{ (sill) May} \sim 1.25 \times 10^{-4} °C \text{ cm}^{-1}$$

$$\frac{\delta T}{\delta Z} \text{ (sill) July} \sim 2.0 \times 10^{-5} °C \text{ cm}^{-1}$$

Average temperature gradient $\sim 7.3 \times 10^{-5}$°C cm^{-1}.

Salt Budget Calculations

The quantities of salt in a 1 cm^2 area of water column bounded by the sill and the basin floor are:

May 325.90 gm cm^{-2}

July 326.72 gm cm^{-2}

Observed rate of change of salt $= \frac{0.82 \text{ gm cm}^{-2}}{45.2 \text{ days}}$

$= 2.1 \times 10^{-7}$ gm cm^{-2} sec^{-1}

Diffusion loss of salt across the sill = -1.4×10^{-7} gm cm^{-2} sec^{-1}.

$\therefore$ rate of salt change due to advection = 3.5×10^{-7} gm cm^{-2} sec^{-1}.

Solution of the budget equation for $\frac{1}{\Delta t}\int_{o}^{h} dZ$

yields a transport: $\frac{3.5 \times 10^{-7} \text{ gm cm}^{-2} \text{ sec}^{-1}}{\rho(32.69 - 32.46)10^{-3} \text{ gm cm}^{-3}}$

$$= 1.54 \times 10^{-3} \text{ cm}^3 \text{ sec}^{-1}$$

which in 45.2 days is equivalent to a water column approximately 6000 cm in height, or approximately 60% of the volume of the water column bounded by the sill and the basin floor. The vertical velocity of water moving into the basin is 1.5×10^{-3} cm sec^{-1}.

Heat Budget Calculations

The quantities of heat contained in a 1 cm^2 area of water column bounded by the sill and the basin floor are:

May 46, 480 cal cm^{-2}

July 47, 300 cal cm^{-2}.

Observed rate of change of heat = $\frac{820 \text{ cal cm}^{-2}}{45.2 \text{ days}}$

$$= 2.1 \times 10^{-4} \text{ cal cm}^{-2} \text{ sec}^{-1}.$$

Diffusion loss of heat across the sill = -2.2×10^{-4} cal cm^{-2} sec^{-1}.

$\therefore$ rate of heat change due to advection = 4.3×10^{-4} cal cm^{-2} sec^{-1}.

Considering the difference in temperatures between the incoming and effluxed water, yields a transport equivalent to:

$$\frac{4.3 \times 10^{-4} \text{ cal cm}^{-2} \text{ sec}^{-1}}{\rho Cp \text{ (4.76 - 4.49) cal cm}^{-3}} = 1.6 \times 10^{-3} \text{ cm}^3 \text{ sec}^{-1}$$

which in 45.2 days is equivalent to a water column approximately 6220 cm in height or approximately 62% of the volume of the water column bounded by the sill and the basin floor. This represents a vertical velocity 1.6×10^{-3} cm sec^{-1}.

Method 2: The advective contribution to the salinity distribution equation is expressed as the product of a vertical advection velocity and an average salinity gradient over the time period of interest. The salinity distribution is expressed:

$$\int_{Z^*}^{sill} \frac{\delta S}{\delta t}\, dZ = W_Z \int_{Z^*}^{sill} \frac{\delta S}{\delta Z}\, dZ - K_Z \int_{Z^*}^{sill} \frac{\delta^2 S}{\delta Z^2}\, dZ.$$

At Z^* ($\Delta\sigma_t = 0$) and $\frac{\delta S}{\delta t}$ at Z^* is approximately zero (density controlled by salinity), and always small compared to $\frac{\delta S}{\delta t}$ evaluated at the sill. The equation after integration and invoking the above reduces to:

$$\frac{\delta S}{\delta t}\, dZ \Big|_{Z^*}^{sill} + K_Z \times \frac{\delta S}{\delta Z} \Big|_{Z^*}^{sill} = W_Z \times \Delta S_{(sill/Z^*)}$$

$\frac{\delta S}{\delta t}$ is the rate of change of salinity.

$\frac{\delta S}{\delta Z}$ is the vertical salinity gradient.

K_Z is the vertical diffusion cofficient.

W_Z is the vertical advection velocity.

$\Delta S_{sill/Z^*}$ is the salinity difference between the sill depth and depth of penetration of the influx.

The term $K_Z\{\frac{\delta S}{\delta Z}(sill) - \frac{\delta S}{\delta Z}(Z^*)\}$ accounts for the salt lost across the

sill corrected for that diffused into the region above Z* from below. Each of the above terms can be evaluated from the time and depth distributions of salinity.

Example: From May CR:155 to July CR:171 1973 (Figs. 4 and 5).

Depth of penetration of influx = 255 m, σ_t^* = 25.91.

dZ = 65 m (190-255 m).

$\frac{\delta S}{\delta t}$ (190 m) $\sim \frac{0.35}{45.2}$ °/₀₀ day = 9.0×10^{-8} °/₀₀ sec^{-1}

$K_Z = 3.0\ cm^2\ sec^{-1}$.

Average $\frac{\delta S}{\delta Z}$ (sill) $\sim 5.5 \times 10^{-5}$ °/₀₀ m^{-1}.

Average $\frac{\delta S}{\delta Z}$ (Z*) $\sim 4.0 \times 10^{-5}$ °/₀₀ m^{-1}

$\Delta S_{sill/Z^*} = 0.30$°/₀₀.

Substitution into the budget equation yields:

$$W_Z \cdot 0.30°/_{00} = 5.8 \times 10^{-4}°/_{00}\ cm\ sec^{-1} + 3\ cm^2\ sec^{-1}\ \{5.5 \times 10^{-5} - 4.0 \times 10^{-5}°/_{00}\ cm^{-1}\} = \frac{6.3 \times 10^{-4}°/_{00}\ cm\ sec^{-1}}{0.30°/_{00}}$$

$$W_Z = 2.1 \times 10^{-3}\ cm\ sec^{-1}\ (1.8\ m\ day^{-1})$$

and is equivalent to a volume in 45.2 days of: $2.1 \times 10^{-3} \times 1.0 \times 45.2 \times 24 \times 3600\ cm^3 = 8201$ and represents approximately 82% of the volume of water contained in a 1 cm^2 column bounded by the sill and the basin floor.

The temperature distributions are expressed similarly:

$$\int_{Z^*}^{sill} \frac{\delta T}{\delta t}\, dZ = W_Z \int_{Z^*}^{sill} \frac{\delta T}{\delta Z}\, dZ - K_Z \int_{Z^*}^{sill} \frac{\delta^2 T}{\delta Z^2}\, dZ.$$

and, after integration the above equation reduces to:

$$W_Z \times \Delta T_{sill/Z^*} = \{\frac{\delta T}{\delta t}\ (sill) - \frac{\delta T}{\delta t}\ (Z^*)\}\ dZ + K_Z\ \{\frac{\delta T}{\delta Z}\ (sill) - \frac{\delta T}{\delta Z}\ (Z^*)\}$$

This is identical to the salinity equation, but the term $\frac{\delta T}{\delta t}\ (Z^*)$ needs to be retained, as temperature does not control density, and the temperature of the incoming water may be quite different from the temperature of the resident basin water at the depth of penetration of the influx.

$$dZ = 65 \text{ m } (190\text{-}255 \text{ m})$$

$$\frac{\delta T}{\delta t}\ (sill) = \frac{0.52°C}{45.2 \text{ day}},\ \frac{\delta T}{\delta t}\ (Z^*) = \frac{0.06\ °C}{45.2 \text{ day}}$$

$$K_Z = 26 \text{ m}^2 \text{ day}^{-1},\ 3 \text{ cm}^2 \text{ sec}^{-1}$$

$$\frac{\delta T}{\delta Z}\ (sill) \sim 6.6 \times 10^{-5} °C \text{ cm}^{-1}$$

$$\frac{\delta T}{\delta Z}\ (Z^*) \sim 40 \times 10^{-5} °C \text{ cm}^{-1}$$

$$\Delta T_{sill/Z^*} = 0.41°C.$$

Substitution into the budget equation yields:

$$W_Z\ 0.41°C = 7.7 \times 10^{-4} °C \text{ cm sec}^{-1} + 3 \text{ cm}^2 \text{ sec}^{-1}$$

$$\{6.6 \times 10^{-5} - 4.0 \times 10^{-5} °C \text{ cm}^{-1}\}$$

$$W_Z = \frac{8.5 \times 10^{-4} \text{ cm sec}^{-1}}{0.41°C}$$

$$= 2.1 \times 10^{-3} \text{ cm sec}^{-1}\ (1.8 \text{ m day}^{-1})$$

and is equivalent to a volume in 45.2 days of:

$$2.1 \times 10^{-3} \times 1.0 \times 45.2 \text{ m}^3 = 8201 \text{ cm}^3$$

and represents approximately 82% of the volume of water contained in a 1 cm^2 column bounded by the sill and the basin floor.

Deep Water Oxygen Consumption Rates: Vertical Advection and Diffusion with Consumption

The oxygen budget for a water column 1 cm^2 in cross-sectional area bounded by the sill and basin floor may be written, assuming that the distributions are a balance between advective processes operating across the sill (these may be positive or negative contributions to the budget depending upon the relative oxygen concentrations of incoming and effluxed basin water), diffusion input across the sill and consumption in the basin.

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta O_2}{\delta t}\, dZ = \frac{1}{\Delta t}\, \{\bar{O}_{2(I)} - \bar{O}_{2(E)}\} \int_{o}^{h} dZ - \int_{\text{bottom}}^{\text{sill}} \frac{\delta}{\delta Z} \left(K_Z \frac{\delta \bar{O}_2}{\delta Z}\right) dZ + \int_{\text{bottom}}^{\text{sill}} R\, dZ$$

where: $\frac{\delta O_2}{\delta t}$ is the observed rate of change of oxygen

$\bar{O}_{2(I)}$ is the average oxygen concentration of incoming water across the sill

$\bar{O}_{2(E)}$ is the average oxygen concentration of resident basin water effluxed due to the advective process

$\frac{\delta O_2}{\delta Z}$ is the vertical oxygen gradient

R is the average oxygen consumption rate in the water column, between the depths of integration.

It has been assumed that there is no flux of oxygen across the basin floor i.e., either K_Z, or $\frac{\delta O_2}{\delta Z} = 0$. The assumption is probably incorrect; the surface sediments of Resurrection Bay are apparently not anoxic and aerobic metabolism of particulate organic matter is proceeding there. This means that the water column consumption rates (R)

given in the text are approximations only; no account of the flux of oxygen from the water column into the surface sediments has been made.

The advective contribution to the budget (the first term on the RHS of the equation) has been written as the product of the difference between the oxygen concentrations of the incoming and effluxed basin water, and a transport volume/time. Because of the intermittent character of the advective exchanges the above is a more accurate representation of the advective contribution, than is the product of the vertical advective velocity (W_Z) and the vertical oxygen gradient ($\frac{\delta O_2}{\delta Z}$). The latter, because principally of the gradient in oxygen concentration (which does not truly represent a balance between advection and consumption, but primarily consumption and diffusion) overestimated water column consumption rates. The concentration of oxygen in the incoming water was interpolated from the vertical distribution at the station beyond the sill (Res-4), at the density corresponding to the density of the incoming water. The average oxygen concentration of the effluxed water was computed from the depth distribution of oxygen inside the inner fjord basin, prior to the influx, from the sill to the depth of the influx. When no advection to the basin was identified, the term was dropped from the equation.

The observed rate of change of oxygen (term on the LHS of the equation) was evaluated by numerically integrating the depth distribution of oxygen between the sill and the basin floor. The distance between the sill depth and the basin floor was divided into 5 segments of 20 m depth each, and assuming the concentration of oxygen at the

mid-point of each depth interval representative of the average concentration of that interval.

The diffusive contribution, because of the lower boundary condition of no oxygen flux into the sediment, reduces to the product of the vertical eddy mixing coefficient and the vertical oxygen gradient across the sill.

Example: November, CR:182 through December CR:183, 1973

Depth of penetration of influx = 220 m, σ_t = 26.17

Volume of water exchanged = 48% of basin volume

Oxygen concentration of incoming water = 4.08 ml ℓ^{-1}

Oxygen concentration of effluxed water = 4.30 ml ℓ^{-1}

Observed rate of change of oxygen in the basin = -8.2×10^{-2} ml cm^{-2} day^{-1}

Change due to advection = -3.4×10^{-2} ml cm^{-2} day^{-1}

Change due to diffusion = 6.6×10^{-2} ml cm^{-2} day^{-1}

$\therefore$ net consumption = -1.14×10^{-1} ml cm^{-2} day^{-1}

$= 4.2$ ml ℓ^{-1} yr^{-1}.

APPENDIX B

Optimum Analysis Conditions

The following tests were carried out in a seawater sample filtered through a 0.4 μm Nuclepore membrane and acidified to pH ∿ 2.5. The sample contained approximately 10^{-8} mole ℓ^{-1} copper ion. The variations in the oxidation current peak height were and oxidation peak potentials were monitored as each of the succeeding instrumental parameters were varied while other operating conditions were maintained constant. The results are summarized in Figure 1. The conditions used for analyses are indicated with arrows.

Modulation Amplitude

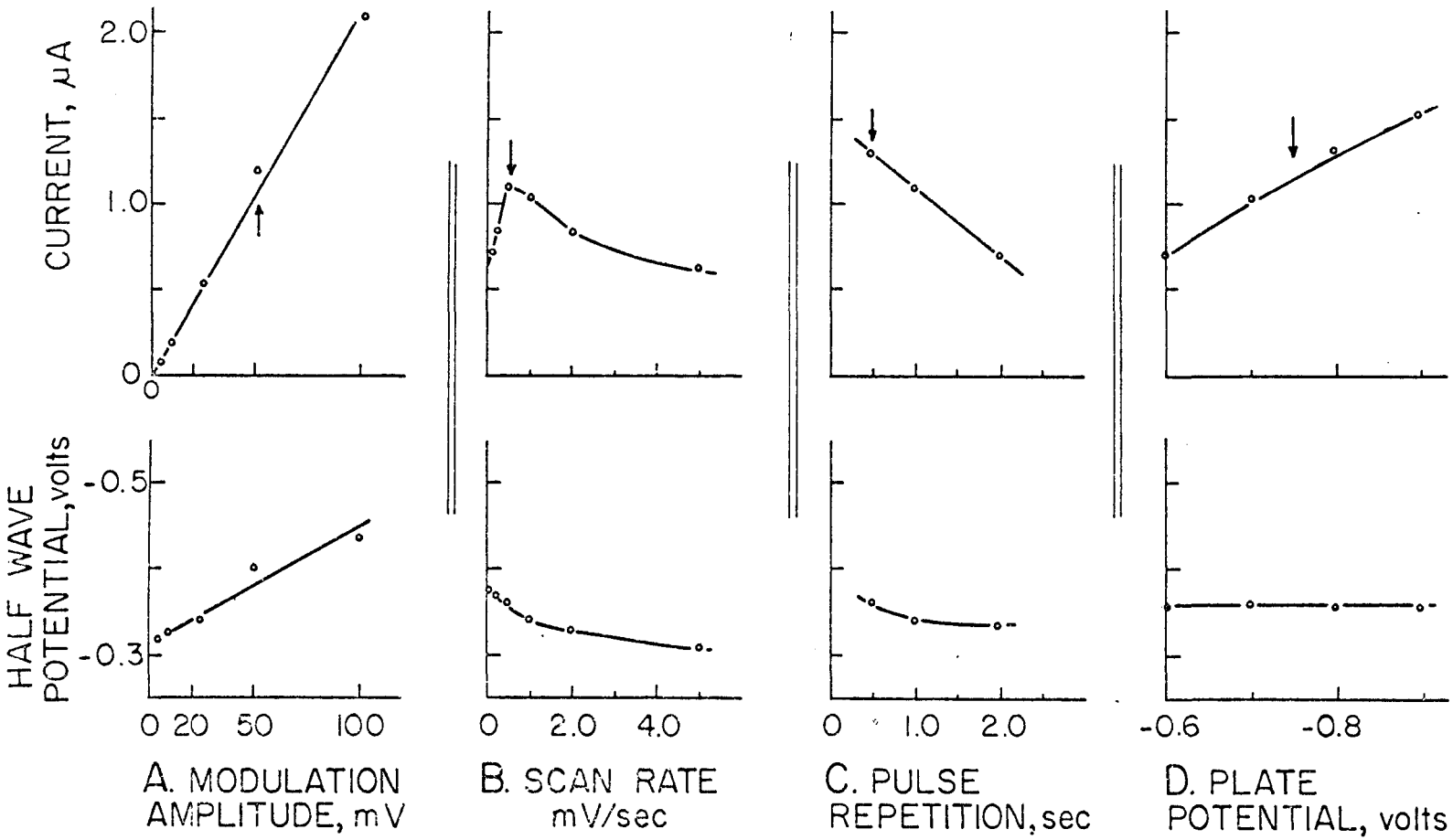
Peak current increased and half-wave potential moved in a more negative direction as the modulation amplitude was increased. Although highest peak currents were obtained at 100 mV pulse, the copper peak was distorted somewhat and a marked increase in the background current slope was observed. All measurements were made using a 50 mV pulse.

Scan Rate

Maximum peak currents were observed with a scan rate of 5 mV sec^{-1}. The resolution of the copper wave was increased at lower scan rates but at 20 mV sec^{-1} and 50 mV sec^{-1} the background current slope increased markedly and the copper wave was poorly resolved.

Pulse Repetition

Of the available machine settings a pulse repetition time of 0.5



Appendix B - Figure 1. Optimum analysis conditions in the differential pulsed mode.

sec produced maximum peak current and sharper peaks.

Plate Potential

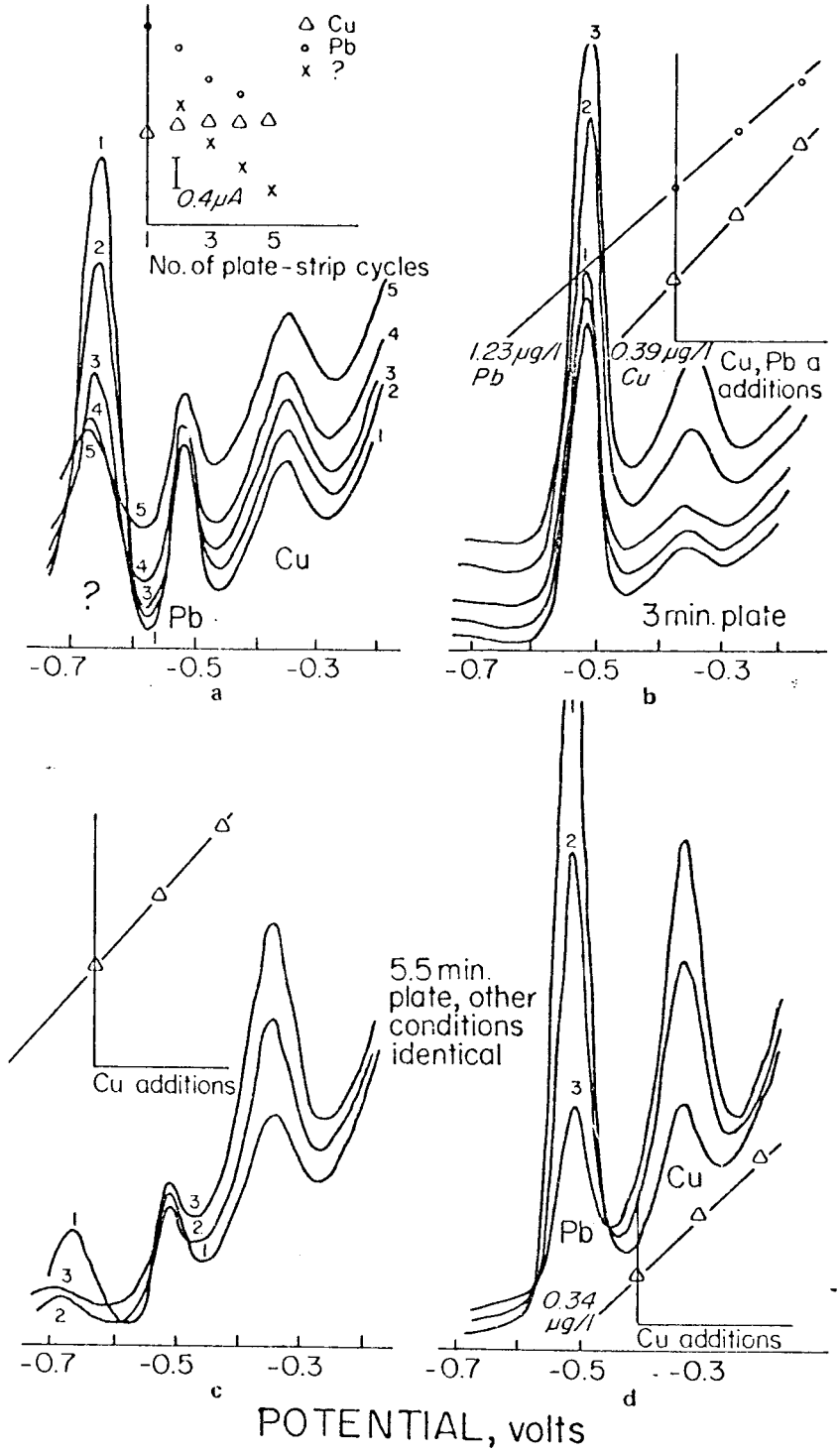
The potential chosen to plate metals into a mercury coated inert electrode must be more negative (cathodic) than the reduction potential of the metal ion of interest. However, it must not be so negative other electrode reactions interfere with the deposition of the metal ion of interest. The effect of the plate potential on the copper wave peak current is shown in Figure 1d. Maximum peak currents were obtained at -0.90V but at more negative potentials in acid solution hydrogen gas was produced at the working electrode and at potentials greater than about -1.2V, copper was interferred with by zinc deposition. The analysis time is increased as the scan range is expanded, and for this reason -0.75V was chosen as the plate potential.

Interference in Lead and Cadmium Analyses

A plate potential of -0.75V was used throughout this work, and at this potential both cadmium and lead were plated into the mercury film. Lead and cadmium were not of specific interest in this study, but in the analyses of several seawater samples some 'curious' behavior of the lead peak was observed and in some samples an irregular peak appeared at about -0.65V, which would have prevented any cadmium determinations. These phenomena are described only briefly here, in that they may be of interest or concern to other persons wishing to determine these metals in seawater. The effect is illustrated in Figure 2a. The samples collected

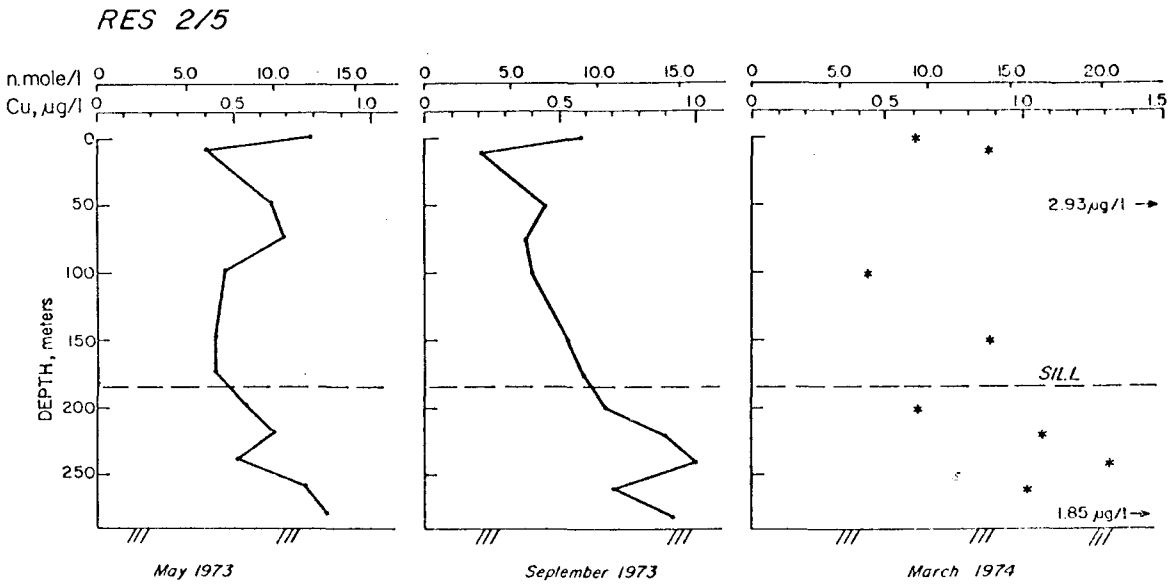
during January and February only of 1975 showed this behavior; it was observed at both stations (Res-2.5 and Res-4) below 100 m during January, but only at Res-4 throughout all of the water column during February. At Res-2.5 during February all samples analyzed demonstrated a normal response to standard lead additions. Some effort was made to determine if this problem was peculiar to specific samples. The following simple tests were carried out. During the analyses of samples from Res-4, February 1975, only one or two samples could be run that demonstrated an expected response to lead standard additions before sensitivity decreased, this persisted with several electrodes. A freshly polished electrode was plated in $\sim$ 0.6 M KCl in the usual fashion and two 'old' samples from the Gulf of Alaska were analyzed for Cu and Pb. Although the concentration of Pb was high (1.23 µg ℓ^{-1}) a linear response to standard additions was found (Fig. 2b). Samples were then analyzed from Res-4 (February 1976) and the 'anomalous' peak at about -0.65V appeared and on successive platings of the same sample both it and the lead peak decreased in intensity, but the copper peak remained constant. The same effects persisted with several other samples, the peak at -0.65V, and the Pb peak eventually disappeared altogether and finally no response to Pb additions was observed (Fig. 2c). Throughout these samples the copper peak increased linearly upon standard additions. The same electrode was left overnight and about twenty-four hours later one of the Gulf of Alaska samples (#33) that had been analyzed previously was reanalyzed; a decreasing lead peak was observed on successive plate-strip cycles and no increase

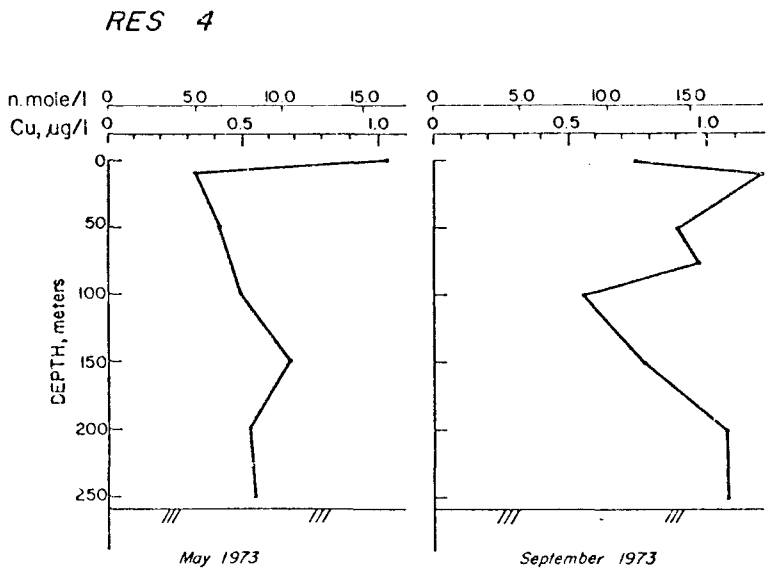
in peak height was observed when standard additions were made to the cell (Fig. 2d). The concentration of copper in the analysis (0.34 μg ℓ^{-1}), when the electrode had been freshly plated with mercury and none of the Resurrection Bay samples had been analyzed. The data suggest there was some material in the samples that interfered with the redox reaction of lead at the electrode surface, hence preventing the quantitative determination of lead. If this behavior was due to surface active compounds in seawater the latter appear to be specific to segments of the water column in Resurrection Bay only during the winter months. During January, advection of water from the Gulf of Alaska penetrated the fjord between about 100 m and 185 m depth (Appendix A; Fig. 2). The apparent deterioration of the lead peak appeared to be associated with the advection process, suggesting some dissolved component peculiar to that water mass, but the source of any such material, if real, remains a mystery.



Appendix B - Figure 2. Apparent interference in lead and cadmium analysis.

APPENDIX C





Appendix C - Figure 1. Depth distributions of copper at Res-2.5 and Res-4 (starred data points are unfiltered samples).

APPENDIX C

TABLE 1

Interstitial Water Copper Concentrations

Date: 25 July 1974

Core 2	
Depth in sediment (cm)	Copper µg ℓ^{-1}
0- 8	9.58
34- 42	2.39
74- 82	2.29
114-121	4.69

Date: 21 October 1974

Core 1		Core 3	
Depth in sediment (cm)	Copper µg ℓ^{-1}	Depth in sediment (cm)	Copper µg ℓ^{-1}
0- 6	6.51	0- 9.5	8.54
14- 20	2.02	12-18.5	1.02
40- 45	2.46	22-29	1.67
111-116	2.53	34-41	3.48

APPENDIX C

TABLE 1 (Continued)

Date: February 1975

Core 1		Core 2	
Depth in sediment (cm)	Copper µg ℓ^{-1}	Depth in sediment (cm)	Copper µg ℓ^{-1}
0 - 4.8	4.90	0 - 4.8	8.48
18.4- 23.5	1.26	7.2-11.5	1.96
39.5- 46.5	sample lost	14.5-19.2	2.80
96 -100	2.45	34 -38	3.28

Date: May 1975

Depth in sediment (cm)	Copper µg ℓ^{-1}
0 - 5	9.98
6.5- 12.5	1.88
14.2- 22.0	1.96
42.0- 47.5	3.36
76 - 83.5	3.83
123 -129	3.12

Deep Water Copper Budget

A budget euqation for copper in the deep water of Resurrection Bay may be written in the following form:

$$\int_{\text{bottom}}^{\text{sill}} \frac{\delta Cu}{\delta t}\, dZ = \{Cu_{(I)} - Cu_{(E)}\} \frac{1}{\Delta t} \int_{o}^{h} dZ - \int_{\text{bottom}}^{\text{sill}} \frac{\delta}{\delta z}\left(K_z \frac{\delta Cu}{\delta z}\right) dZ + \int_{\text{bottom}}^{\text{sill}} J \cdot dZ$$

The terms in the equation are numbered consecutively from left to right. Term (1), represents the observed time rate of change of copper in the water column (assumed 1 cm^2 in cross-sectional area) bounded by the sill depth contour and the sediment surface. The term is evaluated numerically by integrating the depth distribution of copper (between the sill and sediment surface) between any two given measurement periods:

$$\frac{1}{\Delta t} \sum_{i=1}^{i=10} \{Cu_{(t_1)} - Cu_{(t_2)}\}\, dZ_i \ \mu g\ Cu\ cm^{-2}\ sec^{-1}$$

$Cu_{(t_1)}$ is the copper concentration at any given depth, at measurement time (t_1). Measurements of copper in the water column were made predominately at 10 m depth intervals, the concentration was assumed to represent the average concentration of that interval.

Term 2, represents the advective contribution to the observed time rate of change of copper. It represents net additions to or decreases in copper levels, depending upon the relative concentrations of influxed, $Cu_{(I)}$ and effluxed, $Cu_{(E)}$, water and the volume of water

exchanged because of the advection. If no advective influx to the basin was identified, the term was neglected in the budget equation. When advection was identified (indicated when the density of water behind the sill increased), $Cu_{(E)}$ (the average copper concentration of water effluxed from the basin) was calculated by identifying the depth to which the influx penetrated Z* (see Appendix A), integrating the copper concentrations at time (t_1) between this depth and the sill depth and dividing by the volume of water exchanged. $Cu_{(I)}$, the average concentration of copper influxed to the basin was found by interpolation of the depth-distribution of copper at Station Res-4 (fjord source water) at the depth where the density was equal to the density of the water added to the inner basin. These data were combined with the volume of water added to the basin (Chapter 2 - Table 7; Appendix A).

Term 3, represents the diffusive contribution to the copper budget and reduces to the flux of copper across the sill depth by mixing processes and is numerically equal to the product of the average vertical copper gradient across the sill and the eddy mixing coefficient (Chap- 2 - Table 6; Appendix A).

The remaining term (4), represents the copper from term (1), (the observed rate of change of copper in the basin) that cannot be accounted for by advective and/or diffusive contributions. If negative, it represents net losses from the water column and conversely, if positive, it represents net increases in copper in the water column. The net losses or gains may be due to reactions of copper in the water column, i.e. non-conservative behavior, or exchanges across boundaries.

Example: June 28 CR:192 to July 25 CR:195

The hydrographic data indicated that an advective influx into the deep basin occurred during this period, about 20% of the basin water behind the sill was exchanged (Chapter 2).

The average concentration of copper in water displaced from the basin, $Cu_{(E)}$, calculated knowing the depth of penetration of the influx Z*=268m, and the vertical distribution of copper on June 28 at Res-4, was 0.61 $\mu g\ \ell^{-1}$.

The advective contribution to the copper budget:

$$\frac{1}{28}\ (0.64-0.61)\ 10^{-3} \times 2000\ \ \mu g\ Cu\ cm^{-2}\ d^{-1}$$

is numerically equal to 0.06×10^{-3} $\mu g\ Cu\ cm^{-2}\ d^{-1}$ and indicates that copper is added to the basin because of the influx.

The copper gradients across the sill are:

$$\frac{\delta Cu}{\delta Z}\ \text{June} \sim 2.3 \times 10^{-8}\ \mu g\ Cu\ cm^{-4}$$

$$\frac{\delta Cu}{\delta Z}\ \text{July} \sim 5.8 \times 10^{-8}\ \mu g\ Cu\ cm^{-4}$$

Average vertical copper gradient $\sim 4.1 \times 10^{-8}$ $\mu g\ Cu\ cm^{-4}$ and for K_z = 3.5 $cm^2\ sec^{-1}$, the diffusional loss of copper across the sill is

$$-K_z \frac{\delta Cu}{\delta Z}\ (\text{sill}) = 3.5 \times 4.1 \times 10^{-8} = 1.23 \times 10^{-2}\ \mu g\ Cu\ cm^{-2}\ d^{-1}$$

The observed time rate of change of copper in the basin:

$$\frac{1}{\Delta t} \sum_{i=1}^{i=10} (Cu_{t_i} - Cu_{t_2})\ dZ_i = -3.29 \times 10^{-2}\ \mu g\ Cu\ cm^{-2}\ d^{-1}$$

Substituting each of the above into the budget equation, yields an

unaccounted for loss of copper from the water column equal to -2.7×10^{-2} µg Cu cm^{-2} d^{-1}, or -9.9 µg Cu cm^{-2} yr^{-1}.

Example: January CR:204 to February CR:206

Observed time rate of change of copper, Δt=37.2 days is:

$$\frac{1}{\Delta t} \sum_{i=1}^{i=10} (Cu_{(t1)} - Cu_{(t2)}) = 2.9 \times 10^{-2} \text{ µg Cu cm}^{-2} \text{ day}^{-1}$$

Vertical copper gradients across the sill:

$$\frac{\delta Cu}{\delta Z} \text{ (sill)} \quad \text{January} \sim -1.88 \times 10^{-8} \text{ µg Cu cm}^{-4}$$

$$\text{February} \sim -7.14 \times 10^{-9} \text{ µg Cu cm}^{-4}$$

$$\text{Average vertical gradient} \sim -1.29 \times 10^{-8} \text{ µg Cu cm}^{-4}$$

For K_z = 3.5 cm^2 sec^{-1}, the diffusional input of copper into the basin is:

$-3.5 \times -1.29 \times 10^{-8}$ µg Cu cm^{-2} sec^{-1}, or 3.9×10^{-3} µg Cu cm^{-2} d^{-1}.

Solution of the budget equation gives an unaccounted for increase in copper in the basin equal to 2.51×10^{-2} µg Cu cm^{-2} d^{-1}, or 9.2 µg Cu cm^{-2} yr^{-1}.

APPENDIX C

TABLE 2

Summary of Suspended Particle Size Distributions and Types

Reference	Location	Pertinent Data
Gillbricht (1952) (cited in Zeitzschel, 1970)	Baltic Sea	20μ average
Lizitzin (1962) (cited in Zeitzschel, 1970)	Indian Ocean	10-30% of suspended matter (dry weight) was biogenic origin
Mullin (1965)	Indian Ocean	Particulate carbon analyses 58% 1-10 μm 30% 10-95 μm
Hobson (1967)	N.E. Pacific Ocean	90% of total particulate mass in size range 8-44μ 20 to 30% was particulate organic carbon
Sheldon *et al.*, (1967)	Departure Bay and Strait of Georgia B.C. Canada	majority of particles in surface waters (<20m) between 20 and 64 μ and comprised plankton and organic detritus below 50m relative distributions of particles between 2 and 64 μ were about equal; few of the large particles settle into deep water.
Buckley and Loder (1968)	North Dawes Inlet, Alaska	From nine stations average percentage of total particulate matter. 46% 1-10μ 22% 10-25μ
Lenz (1968) (cited in Zeitzschel, 1970)	Baltic Sea	94% of particles 8-30μ Average particle size 17.6μ ($\sigma = \pm$ 6.5μ)
Parsons (1969)	Saanich Inlet B.C. Canada	Early May particulate matter predominately nano-plankton average size 8μ.

APPENDIX C

TABLE 2 (Continued)

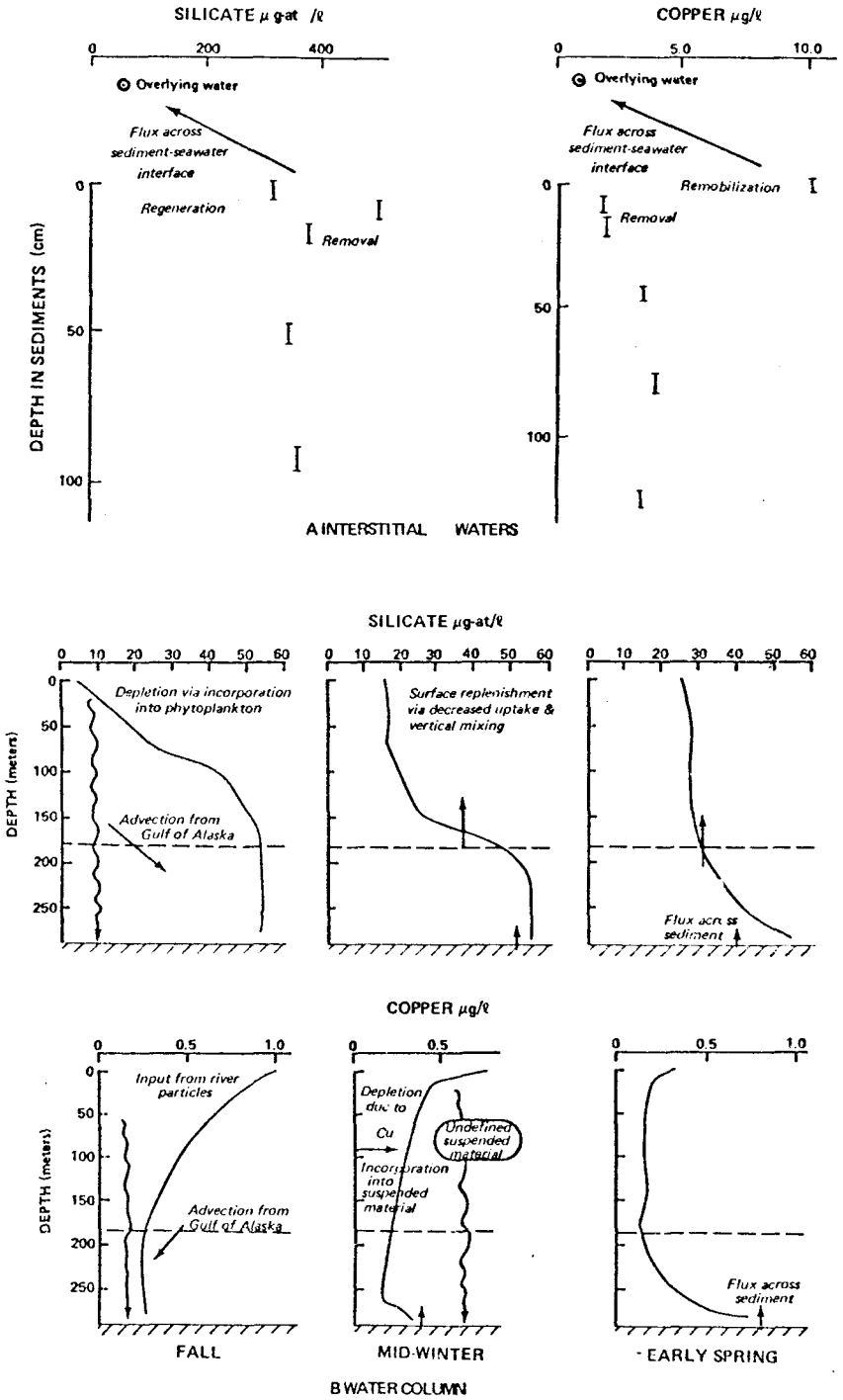
Reference	Location	Pertinent Data
Parsons (cont'd)		End of May microplankton >20μ relatively abundant.
		End of June ultraplankton <2μ increase.
Riley *et al.*, (1965)	Sargasso Sea	Of total dry weight of particulate matter 4.5 to 7.1% was carbon.
Hobson and Menzel (1969)	East coast of South America	5 to 7% of total particulate matter was particulate organic carbon.
Gordon (1970)	North Atlantic Ocean	'Most' particles <28μ, 'majority' of particles <7μ.
		Major particle size class <7μ 'aggregates', were predominately carbohydrate, amorphous and consisted of phytoplankton, bacteria and mineral grains. Next most abundant class (14-28μ) 'flakes' predominately protenaeous material, probably bacteria.
Shaw (1976)	Gulf of Alaska	95-97% of total particulate matter <22.1μ. Data from two stations: 18.5μ dominant size, median 4.8μ; and 10.7μ and 2.8μ dominant, median 3.5μ.

Vertical and Seasonal Variations of Nutrients (N, P, Si) and Copper in the Water Column and Interstitial Waters of Resurrection Bay: Contrasts and Comparisons

The following discussion compares and contrasts the vertical and seasonal variations of copper and oxidized forms of nutrients (N, P, Si) in Resurrection Bay. Similarities infer that the different classes of elements undergo similar processes operating over similar time scales but they do not necessarily mean that nutrients (N, P, Si) and trace metals (copper) originate from the same source nor that they follow identical pathways; reference should be made to Figure 2.

The seasonal variations of nutrients in Resurrection Bay (Heggie *et al.*, 1977), in brief, were found to be principally controlled in summer by phytoplankton growth in surface waters and advection from the Gulf of Alaska in deep waters (>150m) and, during the winter by decreased phytoplankton growth in surface waters, regeneration in bottom waters and surface sediments and vertical mixing processes.

Nutrients (N, P, Si) are depleted in the surface waters of Resurrection Bay during the summer but there does not appear a marked depletion of copper over the same period although copper is 'essential', in that it is required for growth and is found in phytoplankton, e.g., (Knauer and Martin, 1973). The observation does not necessarily mean that copper is not taken up by plants in Resurrection Bay; a rapid turnover time (uptake $\rightleftharpoons$ release) in phytoplankton and/or re-supply of soluble copper into surface waters by a release from particles supplied to the fjord from river runoff would obscure depletion from the water column by plankton uptake.



Appendix C - Figure 2. Representative copper and silicate depth profiles in the water column and interstitial waters during different seasons.

Surface water nutrients increase during the winter as plant growth becomes almost non-existent and vertical mixing processes replace the nutrient depleted surface zones. Copper levels in surface waters in contrast, decrease throughout the winter months indicating decreased supply and/or removal.

The concentrations of nitrate, phosphate and silicate in the deep waters decreased during the winter and spring months by vertical mixing processes. The concentrations of copper are decreased over the same period, but the depletion from these waters of copper cannot be explained by vertical mixing processes. The concave down copper depth profile indicates that the intermediate and deep waters of the fjord would have increased slightly in copper concentrations had concentrations been controlled by physical transport processes only. The observed decreases can only be explained by a removal reaction, and this is to be contrasted to the concave up nutrient depth profiles. The above differences may be explained by the associations that these different elemental types have with particles. Depth distributions of oxidized nutrients are governed principally by biological cycling and undergo relatively little removal below the euphotic zone although phosphate and silicate may be adsorbed onto ferric hydroxides (Stumm and Morgan, 1970). Copper however may be actively taken up by phytoplankton within the euphotic zone and also be passively adsorbed onto particle surfaces by abiotic chemical reactions, e.g. ion-exchange adsorption and inorganic and organic complexation reactions. Because copper concentrations are about two orders of magnitude less in the sea than

nutrients, the latter reactions are a relatively more important control on copper concentrations and distributions.

Although the concentrations of nutrients in the intermediate and deep waters are decreased, the bottom water concentrations are maintained at approximate steady state conditions during the winter; similarly, but more extensively copper concentrations are increased. The interstitial water nutrient and copper concentrations and distributions indicate that the surface sediments are a source of nutrients and of copper for the overlying waters. The enrichments of copper and nutrients in the surface interstitial waters and fluxes into the overlying waters are the result of 'remineralization', and 'remobilization' processes respectively from particles in sediments. The more obvious effect of remobilization processes upon bottom water copper concentrations in winter, probably result from the fact that particle scavenging from the water column has been minimized as particle input to the surface waters has virtually ceased. However, nutrients continue to be transported out of the deep basin by mixing processes.

Biogenic particle production in surface waters and subsequent settling of detritus through the water column may be responsible for the continued loss of copper from the water column during the summer and winter months. The biological oxidation of these particles in the surface sediments may result in the simultaneous release of nutrients and copper in the sediments.

Biogenic Carbon Flux to the Sediment

The biological oxidation of particulate organic material in the ocean has been represented by the equation:

$$R = R_o\, e^{-\alpha z}$$

R = rate of oxidation at any given depth

$$\alpha = \frac{\text{rate of oxidation of particulate organic matter}}{\text{net rate of transport downward}}$$

The rate of oxidation particulate organic carbon was calculated from the rate of oxygen consumption found in the deep water of Resurrection Bay. Using Richard's (1965) equation for the oxidation of 'average' organic matter in the sea, one mole of organic matter requires 138 moles of molecular oxygen.

The average deep water column consumption rate was calculated to be about 3.5 ml $O_2 \ell^{-1}$ yr^{-1} and is equivalent to:

$$\frac{1}{1000}\ \frac{3.5}{22400}\ \times\ \frac{106}{138}\ \times\ ^{12} = 1.45\ 10^{-6}\ \text{gm C cm}^{-3}\ \text{yr}^{-1}$$

Determination of α requires the rate at which particulate carbon is transported downward. For a dominant particle size-class of biogenic material in the ocean between 10-50μ (Appendix C, Table 2), settling velocities range between 6.6×10^{-4} cm sec^{-1} and 5.3×10^{-3} cm sec^{-1} (McCave, 1974, Table 2).

The average concentration of suspended particulate matter in Resurrection Bay was 1.03 mg ℓ^{-1}, therefore the mass flux of particulate carbon (assuming that all the suspended load was of biogenic origin and 20% carbon) through the water column was calculated to vary

between 4.3×10^{-3} and 3.4×10^{-2} g C cm^{-2} yr^{-1}. Values of α therefore were computed to vary between 3.4×10^{-4} and 4.3×10^{-5} cm^{-1}. These values are higher than those cited in Broenkow (1969) of between 0.5 and 4×10^{-5} cm^{-1}. The latter were obtained by curve fitting procedures on depth distributions of both reactants and products of biological oxidation in deep basins. The accuracy of values of α found in this work, although data for biological oxygen consumption, hence carbon oxidation and particulate matter concentrations were available, suffers from a lack of knowledge of particle sizes and settling velocities in Resurrection Bay. These latter determine the mass flux downward - hence the large uncertainty in α. McCave (1974) states an uncertainty of a factor of 3 in computed settling velocities and the average concentration of particulate matter used in these calculations was obtained principally from winter and spring data; the yearly average would probably be somewhat higher.

Variations in α, probably represent the greatest analytical source of error in calculations of carbon flux to the sediment, and therefore of biogenic copper flux to the sediment. For values of α between 3.4×10^{-4} and 4.3×10^{-5} cm^{-1} respectively, carbon fluxes to the sediment (assuming 20% C lost to higher trophic levels) were 234 and 658 mg Cm^{-2} d^{-1} respectively. The corresponding biogenic copper fluxes (Cu:C = 1.6×10^{-3} were between 13.7 and 38.5 µg Cu cm^{-2} yr^{-1} respectively.

APPENDIX C

TABLE 3

Cu:C Ratios (by weight) in Phytoplankton

Reference	Information	Cu:C (weight)
Lowman *et al.*, 1971	Concentration factor 30,000; ave. Cu Res. Bay surface waters $\sim$1.0 μg ℓ^{-1}; C $\sim$2.5 m.mole ℓ^{-1}	2.8×10^{-4}
Boyle & Edmond 1975a	Cu:N surface waters Antarctic convergence	0.8×10^{-4}
Goldberg *et al.*, 1971 (Table 7)	Cu:P ratio in plants	3.2×10^{-4}
Martin & Knauer 1973 Knauer & Martin 1973	Bulk analyses of phytoplankton from, Monterey Bay California, North Pacific Ocean; mean Cu 8.5 μg g^{-1}; diatoms 20% by weight C	0.4×10^{-4}
Spencer & Brewer 1969	Cu:P ratio = 6.5×10^{-3} derived from copper & phosphorus residues in ash; C:P (weight)=44:1.	1.5×10^{-4}

Interstitial Water Copper Concentrations: Control by Solid Sulfide and Carbonate Equilibria or Reactions with Organic Matter

Although hydrogen sulfide in the sediments of Resurrection Bay was not detected via smell nor analysis by the method of Cline (1969), hydrogen sulfide was readily liberated when a little dilute hydrochloric acid was added to raw sediments. Considering the relatively high concentration of iron in the sediments ∿2.0%, the observation suggested that the concentration of sulfide in the interstitial waters was controlled by iron sulfide equilibria. For sulfide ion concentration controlled by iron mineral equilibria, it was examined if, under these conditions the copper concentration in the interstitial water could be explained.

The ultimate stable iron mineral under low Eh and $pS^{=}$ conditions is pyrite Fe S_2. It is formed from metastable mackinawite Fe S and greigite Fe_3 S_4 (Berner, 1971). The sulfide ion concentration can be found from the pyrrhotite-pyrite equilibria and is given by Berner (1971):

$$Fe\ S_{pyrrhotite} + S^{=} \rightleftarrows Fe\ S_{2\ pyrite} + 2e$$

$$Eh = -0.782 + 0.0296\ pS^{=}$$

For values of Eh between about -0.15V and -0.25V $pS^{=}$ value are 21.4 and 18.0, respectively and the free copper concentrations (pK_{CuS} = 35.2) are $10^{-13.8}$M, and $10^{-17.2}$M respectively; considerably less than the concentrations found in Resurrection Bay interstitial waters (∿ 10^{-8}M). Gardner (1974) was able to show that at 10^{-3} mole ℓ^{-1} bisulfide ion concentration ($pS^{=}$=10.5) the concentration of copper in solution could

be increased to about 10^{-8} or 10^{-9}M by the formation of bisulfide and polysulfide complexes. However, at $pS^{=}$=18, pHS^{-}=12 (pH = 7.0, pK_2 (H_2S) = 13.0; Stumm and Morgan, 1970), the concentration of the bisulfide copper complex $Cu(HS)_4^{2-}$, (pK $\sim$ 3.2) formed by the reaction of solid copper sulfide with hydrogen sulfide (Barnes and Czamansky, 1967).

$$Cu\ S + H_2\ S_{(aq)} + 2HS^{-} \rightleftharpoons Cu\ (HS)_4^{2-}$$

is only about 10^{-27}M. Those crude calculations indicate that bisulfide complexes cannot be responsible for the copper concentrations in Resurrection Bay interstitial waters.

Similarly crude calculations indicate that interstitial water copper concentrations are not controlled by equilibria with copper carbonate. Copper carbonate has a solubility product pK_S = 9.6 (Ringbom, 1963), and for the reaction:

$$Cu^{++} + HCO_3^{-} \rightleftharpoons Cu\ CO_3 + H^{+}$$

$$Cu^{++} = \frac{Ks\ [H^{+}]}{[HCO_3^{-}]}$$

At pH values around 7.0, the bicarbonate ion concentration is essentially equal to the carbonate alkalinity, which dominates the titration alkalinity, i.e., from:

$$HCO_3^{-} \overset{Ks}{\rightleftharpoons} CO_3^{=} + H^{+}; \quad pK_2 \sim 10$$

and $Alk = [HCO_3^{-}] + 2\ [CO_3^{=}]$

$$Alk = [HCO_3^{-}]\ \{1 + \frac{2K_2}{H}\}$$

For titration alkalinities in Resurrection Bay sediments of around 10 meq l^{-1} (approximately 20 cm depth) the interstitial water copper concentration is only about 10^{-14} M.

The apparent enhanced solubility of copper in sediments may be due to the effects of 'humic' compounds on solid sulfide phases. Rashid and Leonard (1973), found 'humic' material very effective in mobilizing copper from solid phases and Nissenbaum and Swaine (1976) have shown in recent sediments a strong association of copper with organic material. High molecular weight polymeric 'humic' compounds might be expected to remain behind as sediments are compacted and interstitial waters migrate slowly upward; this reasoning could explain the apparent slight increase with depth observed in Resurrection Bay interstitial water copper concentrations.

Minor Metal Accumulation in Manganese Nodules

Manganese nodules cover large areas of the ocean floor, are known to be formed *in situ via* nucleation and slow growth and contain about 20% by weight of manganese, 15% iron and lesser proportions of several other metals including copper. The primary source, seawater versus interstitial waters of minor metals in nodules has been a puzzle for many years. The data from Resurrection Bay and the demonstration of remobilization processes of copper in surface sediments - a means of concentrating copper in surface interstitial waters - support a hypothesis that minor metals (copper and others that behave similarly) are derived primarily from surface interstitial waters subsequent to

remobilization. Further, copper in the surface interstitial waters is scavenged by manganese derived from the overlying water, and also manganese derived from the sediments precipitating at the sediment-seawater interface subsequent to remobilization at depth in the sediment and migration through the interface. The relative enrichment of copper in deepsea nodules (Table 4), it is proposed may be due, in part, to an inhibition of scavenging in near shore environments because of the relative concentration of organic matter in sediments near continental boundaries.

The above suppositions are supported by some actual physical and chemical observations about nodules.

(1) Copper is associated with manganese phases in the nodules (Cronan 1972; Margolis 1975; Banning 1975).

(2) Physical featuers of nodules (Raab 1972), including:

(a) lumpy surfaces exposed to the sediment surface, that are freshly formed, are high in Cu, Mn, Ni, Mo, and Zn;

(b) relatively smooth surfaces at the top of the nodules are relatively depleted in these elements and;

(c) zonations around the tops and bottoms of the nodules, the bottom center portion is highest in Cu, Mn, Ni, Co and Zn while the outermost portion is lowest in these elements. These indicate that surfaces closest to the source of metals are highest in concentration; - the relative depletions at nodule extremities result from exchange with seawater.

(3) Manganese:copper ratios in nodules (Table 4) indicate the relative enrichment of copper in deep sea nodules, but this may be due to differences, between nearshore and deep sea environments, in the diagenetic remobilization and migration of manganese. Iron may also

be enriched in sediments by diagenetic remobilization but it migrates and is precipitated less readily than manganese (Lynn and Bonatti, 1965). Iron:copper ratios in nodules (Table 4), also indicate a relative enrichment in deep sea nodules. If the iron in nodules is derived from seawater, and is not remobilized iron from sediments, the ratios (Table 4) may in fact be due to differences in minor metal scavenging between deep sea and nearshore, because of the relative concentration of organic matter in nearshore sediments.

These thoughts are not new, regional geochemistries of manganese nodules have been discussed by Price and Calvert (1970), but a process whereby minor metals (specifically copper) could be concentrated and accumulated at the site of nodule growth had not previously been demonstrated. The remobilization of copper from particulate matter in surface sediments, found in this work, is a process where minor metals (copper at least) may be concentrated at the sediment surface in the dissolved state and subsequently scavenged by precipitating manganese oxides.

APPENDIX C

TABLE 4

Summary of Mn:Cu and Fe:Cu Ratios in Manganese Nodules from Various Locations

Location	Mn:Cu	Fe:Cu
Baltic Sea, circum-gothland region	2919	4681
Eastern Baltic Sea	1132	2427
Black Sea	1725	6668
Atlantic Ocean	85	97
Pacific Ocean	46	26
Above data sources quoted in Price and Calvert 1970 p. 147		
Swedish Lake ores	1525	12730
Atlantic Ocean	109	138
Data and sources from Price 1967 p. 56.		
Loch Fyne, Scotland	13050	1775
Eastern Pacific Continental borderland	397-652	23
Eastern Pacific borderland seamount province	149-480	305
Ave deep sea nodule	55.3	43
Above data and sources quoted in Glasby *et al.* 1971 p. 1182		
*Jervis Inlet, Canada	3765-6155	1429-786
#Canada Freshwater Lakes	30340	20270

*Grill *et al.*, 1968

#Harris and Troup, 1969

REFERENCES

Abdullah, M. I., L. G. Royle, and A. W. Morris. 1972. Heavy metal concentrations in coastal waters. *Nature* 234:158-160.

Alexander, J. E. and E. F. Corcoran. 1967. The distribution of copper in tropical seawater. *Limnology and Oceanography* 12:236-242.

Anderson, J. J. and A. H. Devol. 1973. Deep water renewal in Saanich Inlet, an intermittently anoxic basin. *Estuarine and Coastal Marine Science* I:1-10.

Bakun, A. 1973. Coastal Upwelling Indices West Coast of North America (1946-1971). NOAA Technical Report NMFS SSFR-671.

Banning, D. L. 1975. Copper-nickel-cobalt associations in marine manganese nodules (Abstract). *EOS - Transactions American Geophysical Union* 56:1000.

Barnes, C. A. and E. E. Collias. 1958. Some considerations of oxygen utilization rates in the Puget Sound. *Journal of Marine Research* 17:68-80.

Barnes, H. L. and Czamanske. 1967. Solubilities and transport of ore minerals. In: *Geochemistry of Hydrothermal Ore Deposits*, A. L. Barnes, ed. Holt, Rinehart and Winston.

Barber, R. T. and J. A. Ryther. 1969. Organic chelators: factors affecting primary production in the Cromwell Current upwelling. *Journal of Experimental Marine Biology and Ecology* 3:191-199.

Barber, R. T., R. C. Dugdale, J. J. MacIsaac, and R. L. Smith. 1971. Variations in phytoplankton growth associated with the source and conditioning of upwelling water. *Investigacion Pesquera* 35:171-193.

Barber, R. T. 1973. Organic ligands and phytoplankton growth in nutrient-rich seawater. In: *Trace Metals and Metal-Organic Interactions in Natural Waters*, P. C. Singer, ed. Ann Arbor Science, Inc., Ann Arbor, Michigan. pp. 321-338.

Bender, M. L. and C. Gagner. 1976. Dissolved copper, nickel and cadmium in the Sargasso Sea. *Journal of Marine Research* 34:327-339.

Benninger, L. K., D. M. Lewis and K. K. Turekian. 1975. The use of natural lead-210 as a heavy metal tracer in the river-estuarine system. In: *Marine Chemistry in the Coastal Environment*, T. M. Church ed. American Chemical Society Symposium Series 18, American Chemical Society, Washington, D.C. pp. 202-210.

Berner, R. L. 1971. *Principles of Chemical Sedimentology*. International series in the Earth and Planetary Sciences. McGraw Hill Publishing Company. 240 pp.

Boström, K., C. Moore and O. Joensuu. 1975. Plankton: Chemical composition and significance as a sediment source (Abstract). *EOS-Transactions American Geophysical Union* 56:1006.

Boyle, E., R. Collier, A. T. Dengler, J. M. Edmond, A. C. Ug, and R. F. Stallard. 1975. On the chemical mass-balance in estuaries. *Geochimica et Cosmochimica Acta*. 8:394-410.

Boyle, E. A. and J. M. Edmond. 1975a. Copper in surface waters south of New Zealand. *Nature* 253:107-109.

Boyle, E. A. and J. M. Edmond. 1975b. Determination of trace metals in aqueous solution by APDC chelate co-precipitation. In: *Analytical Methods in Oceanography*, T. R. P. Gibb, Jr., (ed.) American Chemical Society Series, No. 147, American Chemical Society, Washington, D.C. pp. 44-55.

Bradford, W. L. 1972. Study of the chemical behaviour of zinc in the Chesapeake Bay water using anodic stripping voltammetry. Chesapeake Bay Institute, Johns Hopkins University. Technical Report 76. Reference 72-7, Baltimore Maryland. 103 pp.

Breck, W. G. 1975. Redox levels in the sea. In: *The Sea*, E. D. Goldberg, ed.) Vol. 5, John Wiley and Sons, New York. pp. 153-179.

Brewer, P. G. and D. W. Spencer. 1970. Trace element intercalibration study. Unpublished manuscript, Woods Hole Oceanographic Institution. Reference No. 70-62.

Brewer, P. G., D. W. Spencer, and D. E. Robertson. 1972. Trace element profiles from Geosecs II - test station in the Sargasso Sea. *Earth and Planetary Science Letters*. 16:111-116.

Brewer, P. G. 1975. Minor elements in seawater. In: *Chemical Oceanography*, J. P. Riley and G. Skirrow, eds. Vol. 1, 2nd Edition. Academic Press, London. pp. 415-496.

Brinckman, F. E. and W. P. Iverson. 1975. Chemical and bacterial cycling of heavy metals in the estuarine system. In: *Marine Chemistry in the Coastal Environment*, T. M. Church, ed. American Chemical Society Symposium, Series 18. American Chemical Society, Washington, D.C. pp. 319-342.

Broecker, W. S. 1974. *Chemical Oceanography*. Harcourt Brace Jovanovich, Inc., New York. 214 pp.

Broenkow, W. 1969. The distributions of non-conservative solutes related to the decomposition of organic material in anoxic marine basins. Ph.D. Thesis, Univ. Washington. 196 pp.

Brooks, R. R., B. J. Presley and I. R. Kaplan. 1967. APDC-MIBK extraction system for the determination of trace elements in saline waters by atomic absorption spectrophotometry. *Talanta* 14:809-816.

Brooks, R. R., B. J. Presley, and I. R. Kaplan. 1968. Trace elements in the interstitial waters of marine sediments. *Geochimica et Cosmochimica Acta* 32:397-414.

Buckley, D. E. and T. C. Loder. 1968. Particulate organic-inorganic geochemistry of a glacial fjord. (Unpublished manuscript). In: *Clay inorganic and organic inorganic associations in aquatic environments*. Progress report to the United States Atomic Energy Commission (Part 1), Institute of Marine Science, University of Alaska, Fairbanks.

Burrell, D. C. 1975. *Atomic spectrometric analysis of heavy-metal pollutants in water*. Ann Arbor Science, Ann Arbor, Michigan. 331 pp.

Callander, E. 1976. Transition metal geochemistry of interstitial fluids extracted from manganese nodule-rich pelagic sediments of the northeastern equatorial Pacific Ocean. In: *Book of Abstracts Joint Oceanographic Assembly*. Edinburgh, Scotland, September 14-23.

Calvert, S. E. and N. B. Price. 1972. Diffusion and reaction profiles of dissolved manganese in the pore waters of marine sediments. *Earth and Planetary Science Letters* 16:245-249.

Cannon, G. 1973. Observations of bottom-water flushing in a fjord-like estuary. *Estuarine and Coastal Marine Science* 3:95-102.

Chester, R. and M. J. Hughes. 1967. A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. *Chemical Geology* 2:249-262.

Chow, T. J. and T. G. Thompson. 1954. Seasonal variations in the concentration of copper in the surface waters of the San Juan Channel. *Journal of Marine Research* 13:233-244.

Chow, T. J. and C. C. Patterson. 1962. The occurrence and significance of lead isotopes in pelagic sediments. *Geochimica et Cosmochimica Acta* 26:263-308.

Christian, G. D. 1969. Anodic stripping pulse voltammetry. *Journal of Electroanalytical Chemistry* 23:1-7.

Christie, J. A., J. G. Osteryoung and R. A. Osteryoung. 1973. Instrumental artifacts in differential pulse polarography. *Analytical Chemistry* 45:210-215.

Cline, J. D. 1969. Spectrophotometric determination of hydrogen sulfide in natural waters. *Limnology and Oceanography* 14:454-458.

Coonley, L. S., Jr., E. B. Baker and H. D. Holland. 1971. Iron in the Mullica River and Great Bay, New Jersey. *Chemical Geology* 7:51-63.

Copeland, T. R., J. H. Christie, R. A. Osteryoung, and R. K. Skogerboe. 1973a. Analytical applications of pulsed voltammetric stripping at thin film mercury electrodes. *Analytical Chemistry* 45:2171-2174.

Copeland, T. R., J. H. Christie, R. A. Osteryoung, and R. K. Skogerboe. 1973b. Effect of supporting electrolyte concentration in pulsed stripping voltammetry at the thin film mercury electrode. *Analytical Chemistry* 45:995-996.

Craig, H. 1969. Abyssal carbon and radiocarbon in the Pacific. *Journal of Geophysical Research* 74:5491-5506.

Craig, H., S. Krishnaswami and B. L. K. Somayajulu. 1973. ^{210}Pb-^{226}Ra: Radioactive disequilibrium in the deep sea. *Earth and Planetary Science Letters* 17:295-305.

Craig, H. 1974. A scavenging model for trace elements in the deep sea. *Earth and Planetary Science Letters* 23:149-159.

Cronan, D. S. 1972. Regional geochemistry of ferromanganese nodules in the world ocean. In: *Ferromanganese Deposits on the Ocean Floor*, D. R. Horn, ed. Papers from a conference, Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York, 20-22 January. pp. 19-30.

Duchart, P., S. E. Calvert and N. B. Price. 1973. Distribution of trace metals in the pore waters of shallow water marine sediments. *Limnology and Oceanography* 18:605-610.

Durum, W. H. and J. Haffty. 1963. Implications of the minor element content of some major streams of the world. *Geochimica et Cosmochimica Acta*. 27:1-12.

Dyrssen, D. and M. Wedborg. 1974. Equilibrium calculations of the speciation of elements in seawater. In: *The Sea*, E. D. Goldberg, ed. Vol. 5, John Wiley and Son, New York. pp. 181-195.

Ehrlich, H. L. 1972. The role of microbes in manganese nodule genesis and degradation. In: *Ferromanganese deposits on the ocean floor*. D. R. Horn, ed. Papers from a conference, Lamont-Doherty Geological observatory, Columbia University, Palisades, New York, 20-22 January. pp. 63-70.

Erickson, P. E. 1973. The voltammetric determination of copper and lead in seawater: Applications to Indian Arm and Burrard Inlet. M.S. Thesis, University of British Columbia, Canada. 84 pp.

Evans, D. W. and N. H. Cutshall. 1973. Effects of ocean water on the soluble-suspended distribution of Columbia River radionuclides. In: *Radioactive contamination of the marine environment*. Proceedings of a symposium, Seattle, 10-14 July 1972. International Atomic Energy Agency, Vienna. pp. 125-140.

Fanning, K. A. and M. E. Q. Pilson. 1972. A model for the anoxic zone of the Cariaco Trench. *Deep-Sea Research* 19:847-863.

Feely, R. A., G. J. Masseth, and W. M. Landing. 1976. Factors controlling the trace element composition of suspended matter from the northeast Gulf of Alaska (Abstract). *EOS-Transactions American Geophysical Union* 57:93.

Flato, J. B. 1972. The renaissance in polarographic and voltammetric analysis. *Analytical Chemistry* 44:75A-87A.

Florence, T. M. 1970. Anodic stripping voltammetry with a glassy carbon electrode mercury-plated *in situ*. *Journal of Electroanalytical Chemistry* 27:273-281.

Florence, T. M. 1972. Determination of trace metals in marine samples by anodic stripping voltammetry. *Journal of Electroanalytical Chemistry* 35:237-245.

Gade, H. G. 1970. Hydrographic investigations in the OsloFjord, a study of water circulation and exchange processes. University of Bergen, Norway Geophysical Institute Report No. 24.

Gardner, L. R. 1974. Organic versus inorganic trace metal complexes in sulfidic marine waters - some speculative calculations based on available stability constants. *Geochimica et Cosmochimica Acta*. 38:1297-1302.

Gibbs, R. J. 1973. Mechanisms of trace metal transport in rivers. *Science* 180:71-73.

Glasby, G. P., J. S. Tooms, and J. R. Cann. 1971. Geochemistry of manganese encrustacions from the Gulf of Aden. *Deep-Sea Research* 18:1179-1187.

Goldberg, E. D. 1954. Marine Geochemistry I - Chemical scavengers of the sea. *Journal of Geology* 62:249-265.

Goldberg, E. D. 1965. Minor elements in seawater. In: *Chemical Oceanography*, J. P. Riley and G. Skirrow, eds. Vol. 1, 1st edition, Academic Press, London. pp. 163-196.

Goldberg, E. D. 1975. Assessing potential ocean pollutants. National Academy of Sciences, Washington, D.C. 438 pp.

Goldberg, E. D. and G. O. S. Arrhenius. 1958. Chemistry of Pacific pelagic sediments. *Geochimica et Cosmochimica Acta* 13:153-212.

Goldberg, E. D., W. S. Broecker, M. G. Gross, and K. K. Turekian. 1971. Marine chemistry. In: *Radioactivity in the marine environment*, National Academy of Sciences, Washington, D.C. pp. 137-146.

Goldschmidt, V. M. 1937. The principles of distribution of chemical elements in minerals and rocks. *Journal Chemical Society*. 655-672.

Gordon, D. C., Jr. 1970. A microscopic study of organic particles in the North Atlantic Ocean. *Deep-Sea Research* 17:175-185.

Grill, E. V., J. W. Murray and R. D. MacDonald. 1968. Todorokite in Manganese Nodules from a British Columbia Fjord. *Nature* 219: 358-359.

Harris, R. C. and A. G. Troup. 1969. Freshwater Ferromanganese concretions: chemistry and internal structure. *Science* 166:604-606.

Heggie, D. T. 1977. Deep water current measurements in Resurrection Bay: An Alaskan fjord. (Unpublished manuscript), University of Alaska, Fairbanks.

Heggie, D. T., D. W. Boisseau and D. C. Burrell. 1977. Hydrography nutrient chemistry and primary productivity of Resurrection Bay, Alaska, 1972-1975. Institute of Marine Science Report No. 77-2, Sea Grant Report No. 77-9, University of Alaska, Fairbanks, Alaska.

Hobson, L. A. 1967. The seasonal and vertical distribution of suspended particulate matter in an area of the Northeast Pacific Ocean. *Limnology and Oceanography* 12:642-649.

Hobson, L. A., and D. W. Menzel. 1969. The distribution and chemical composition of organic particulate matter in an area of the Northeast Pacific Ocean. *Limnology and Oceanography* 14:159-163.

Hutchinson, G. E. 1957. *A Treatise on Limnology*. Vol. 1, part 2, John Wiley and Sons, New York. 1015 pp.

Jackson, G. A. and J. J. Morgan. 1975. Theory of chelator-metal ion interaction and phytoplankton growth. Unpublished manuscript. W. M. Keck Laboratory of Environmental Engineering Science. California Institute of Technology.

Jenne, E. A. 1968. Controls on Mn, Fe, Co, Ni, Cu, and Zn concentrations in soils and water: the significant role of hydrous Mn and Fe oxides. In: *Trace Inorganics in Water*, R. F. Gould, ed. Advances in Chemistry Series 73, American Chemical Society, Washington, D.C. pp. 337-387.

Kastner, M. 1976. Trace element chemistry of diatoms and radiolarians. In: *Book of Abstracts Joint Oceanographic Assembly*. Edinburgh Scotland, 13-24 September.

Kemula, W. and Z. Kublik. 1963. Application of hanging mercury drop electrodes in analytical chemistry. In: *Advances in Analytical Chemistry and Instrumentation*, C. N. Reilley, ed. John Wiley and Son Inc., Vol. 2, New York. pp. 123-177.

Kharkhar, D. P., K. K. Turekian, and K. K. Bertine. 1968. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium, and cesium to the oceans. *Geochimica et Cosmochimica Acta* 32:285-298.

Knauer, G. A. and J. H. Martin. 1973. Seasonal variations of cadmium, copper, manganese, lead, and zinc in water and phytoplankton in Monterey Bay, California. *Limnology and Oceanography* 18:597-604.

Krauskopf, K. B. 1956. Factors controlling the concentrations of thirteen rare metals in sea-water. *Geochimica et Cosmochimica Acta* 9:1-32.

Kriss, A. E. 1963. *Marine microbiology, Deep Sea* - 1st edition. Oliver and Boyd, London. 536 pp.

Krom, M. D. 1976. Chemical speciation and diagenetic reactions at the sediment-water interface in a Scottish fjord. In: *Book of Abstracts Joint Oceanographic Assembly*. Edinburgh, Scotland, 13-24 September.

Ku, T. L. and W. S. Broecker. 1969. Radiochemical studies on manganese nodules of deep-sea origin. *Deep-Sea Research*. 16:625-637.

Lewis, A. G. and P. H. Whitfield. 1974. The biological importance of copper in the sea. Final report International Copper Research Association Inc., No. 223 New York.

Li, Y. H., J. Bischoff and G. Mathieu. 1969. The migration of manganese in the Arctic Basin sediment. *Earth and Planetary Science Letters* 7:265-270.

Lowman, F. G., T. R. Rice and F. A. Richards. 1971. Accumulation and redistribution of radionuclides by marine organisms. In: *Radioactivity in the Marine Environment*. National Academy of Sciences, Washington, D.C. pp. 161-199.

Lynn, D. C. and E. Bonatti. 1965. Mobility of manganese in the diagenesis of deep-sea sediments. *Marine Geology* 3:457-474.

Margolis, S. V. 1975. Microchemical variations in manganese nodules from the northeastern equatorial Pacific (Abstract). *EOS-Transactions American Geophysical Union* 56:1000.

Martin, J. H. 1970. The possible transport of trace metals via molted copepod exoskeletons. *Limnology and Oceanography* 15:756-761.

Martin, J. H. and G. A. Knauer. 1973. The elemental composition of plankton. *Geochimica et Cosmochimica Acta* 37:1639-1653.

Martin, J. M., J. Jednacak, and V. Pravdić. 1970. The phisico-chemical aspects of trace element behavior in estuarine environments. Lecture paper presented by V. Pravdić and J. M. Martin at the International Symposium on the Chemistry of the Mediterranean, held at the Center for Marine Research, 'Rudjer Bosković' Institute Rovenj, Croatia, Yugoslavia, September 24-26, 1970.

Matson, W. R., D. K. Roe and D. E. Carritt. 1965. Composite graphitie mercury electrode for anodic stripping voltammetry. *Analytical Chemistry* 37:1594-1595.

McCave, I. N. 1975. Vertical flux of particles in the ocean. *Deep-Sea Research* 22:491-502.

Mechalas, B. J. 1974. Pathways and environmental requirements for biogenic gas production in the ocean. In: *Natural Gases in Marine Sediments*, I. R. Kaplan, ed. Marine Science Vol. 3. Plenum Press, New York. pp. 11-25.

Morgan, J. J. 1967. Chemical equilibria and kinetic properties of manganese in natural waters. In: *Principles and Applications of Water Chemistry*, S. D. Faust and J. F. Hunter, eds. John Wiley and Sons, New York. pp. 561-624.

Morgan, J. J. and T. H. Sibley. 1975. Chemical models for metals in coastal environments. Paper presented at American Society Civil Engineering Symposium on Ocean Engineering, April, 1975, Delaware.

Mullin, M. M. 1965. Size fractionation of particulate organic carbon in the surface waters of the western Indian Ocean. *Limnology and Oceanography* 10:453-462.

Myers, D. J. and J. Osteryoung. 1974. Amperometric titrations employing differential pulse polarography. *Analytical Chemistry* 46:356-359.

Nebert, D. L. 1972. A proposed circulation model for Endicott Arm, an Alaskan fjord. M.Sc. Thesis, University of Alaska, Fairbanks. 90 pp.

Nissenbaum, A. and D. J. Swaine. 1976. Organic matter-metal interactions in recent sediments: the role of humic substances. *Geochimica et Cosmochimica Acta* 40:809-816.

Osteryoung, J. G. and R. A. Osteryoung. 1972. Pulse polarographic analysis of toxic heavy metals. *American Laboratory* (July).

O'Connor, T. P. and D. R. Kester. 1975. Adsorption of copper and cobalt from fresh and marine systems. *Geochimica et Cosmochimica Acta* 39:1531-1543.

Parry, E. P. and R. A. Osteryoung. 1965. Evaluation of analytical pulse polarography. *Analytical Chemistry* 37:1634-1637.

Parsons, T. R. 1969. The use of particle size spectra in determining the structure of a plankton community. *Journal Oceanographical Society of Japan* 25:172-181.

Presley, B. J., Y. Kolodny, A. Nissenbaum, and I. R. Kaplan. 1972. Early diagenesis in a reducing fjord, Saanich Inlet, British Columbia - Trace element distribution in interstitial water and sediment. *Geochimica et Cosmochimica Acta* 36:1073-1090.

Preston, A., D. F. Jefferies, J. W. R. Dulton, E. R. Harvey and A. K. Steele. 1972. British Isles coastal waters: The concentrations of selected heavy metals in seawater suspended matter and biological indications. A pilot survey. *Environmental Pollution* 3:69-82.

Price, N. B. 1967. Some geochemical observations on manganese - iron oxide nodules from different depth environments. *Marine Geology* 5:511-538.

Price, N. B. and S. E. Calvert. 1970. Compositional variation in Pacific Ocean ferromanganese nodules and its relationship to sediment accumulation rates. *Marine Geology* 9:145-171.

Price, N. B. and S. E. Calvert. 1973. A study of the geochemistry of suspended particulate matter in coastal waters. *Marine Chemistry* 1:169-189.

Raab, W. 1972. Physical and chemical features of Pacific Deep Sea manganese nodules and their implications to the genesis of nodules. In: *Ferromanganese deposits on the ocean floor*. D. R. Horn, ed. Papers from a conference, Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York, 20-22 January. pp. 31-50.

Rashid, M. A. and J. D. Leonard. 1973. Modifications in the solubility and precipitation behavior of various metals as a result of their interaction with sedimentary humic acid. *Chemical Geology* 11:89-97.

Rattray, M., Jr. 1967. Some aspects of the dynamics of circulation in fjords. In: *Estuaries*, C. H. Lauff, ed. American Association for the Advancement of Science Publication No. 83. Washington, D.C. pp. 52-62.

Reeburgh, W. S. 1967. An improved interstitial water sampler. *Limnology and Oceanography* 12:163-165.

Reeburgh, W. S., R. D. Muench and R. T. Cooney. 1976. Oceanographic conditions during 1973 in Russell Fjord, Alaska. *Estuarine and Coastal Marine Science* 4:129-145.

Reilley, C. N. and W. Stumm. 1962. Adsorption in polarography. In: *Progress in Polarography*, P. Zuman and I. M. Kolthoff, eds. Vol. 1. John Wiley and Sons, QD 115, Institute of Marine Science, University of Alaska, Fairbanks. John Wiley and Sons. p. 68.

Richards, F. A. 1965. Anoxic basins and fjords. In: *Chemical Oceanography*, J. P. Riley and G. Skirrow, eds. Vol. I, 1st edition. Academic Press, London. pp. 611-645.

Rickard, D. T. 1970. The chemistry of copper in natural aqueous solutions. Stockholm Contributions in Geology 23(1):64 pp.

Riley, G. A., P. J. Wangersky, and D. V. Hemert. 1965. Organic aggregates in surface and deep waters of the Sargasso Sea. *Limnology and Oceanography* 10:354-364.

Riley, J. P. and D. Taylor. 1968. Chelating resins for the concentration of trace elements from seawater and their analytical use in conjunction with atomic absorption spectrophotometry. *Analytica Chimica Acta* 40:479-485.

Ringbom, A. 1963. *Complexation in Analytical Chemistry*. John Wiley and Sons, New York. 395 pp.

Robertson, D. E. 1968. Role of contamination in trace element analysis of seawater. *Analytical Chemistry* 40:1067-1072.

Robertson, D. E. and R. Carpenter. 1976. Activation analysis. In: *Strategies for Marine Pollution Monitoring*, E. D. Goldberg, ed. John Wiley and Sons, New York. pp. 93-156.

Roe, D. K. and J. E. Toni. 1965. An equation for anodic stripping curves of thin mercury film electrodes. *Analytical Chemistry* 37:1480.

Royer, T. C. 1975. Seasonal variations of waters in the northern Gulf of Alaska. *Deep-Sea Research* 22:403-416.

Seitz, W. R. 1970. Trace metal analysis by anodic stripping voltammetry. Ph.D. Thesis. Massachusetts Institute of Technology.

Shaw, D. G. 1976. Hydrocarbons: Natural distribution and dynamics on the Alaskan outer continental shelf. Unpublished manuscript. Institute of Marine Science, University of Alaska, Fairbanks. 123 pp.

Sheldon, R. W., T. P. T. Evelyn, and T. R. Parsons. 1967. On the occurrence and formation of small particles in seawater. *Limnology and Oceanography* 12:367-375.

Sholkovitz, E. R. and J. M. Gieskes. 1971. A physical-chemical study of the flushing of the Santa Barbara basin. *Limnology and Oceanography* 16:479-489.

Shuman, M. S. and G. P. Woodward, Jr. 1973. Chemical constants of metal complexes from a complexometric titration followed with anodic stripping voltammetry. *Analytical Chemistry* 45:2032-2035.

Sibley, T. H. and J. J. Morgan. 1975. Equilibrium speciation of trace metals in freshwater:seawater mixtures. Unpublished manuscript. W. M. Keck Laboratory of Environmental Engineering Science, California Institute of Technology.

Siegerman, H. and G. O'Dom. 1972. Differential pulse anodic stripping of trace metals. *American Laboratory* (June).

Slowey, J. F. and D. W. Hood. 1971. Copper, manganese and zinc concentrations in Gulf of Mexico waters. *Geochimica et Cosmochimica Acta* 35:121-138.

Spencer, D. W. and P. G. Brewer. 1969. The distribution of copper, zinc, and nickel in seawater of the Gulf of Maine and the Sargasso Sea. *Geochimica et Cosmochimica Acta* 33:325-339.

Spencer, D. W., D. E. Robertson, R. K. Turekian and T. R. Folsom. 1970. Trace element calibrations and profiles at the Geosecs test station in the northeast Pacific Ocean. *Journal of Geophysical Research* 75:7688-7696.

Spencer, D. W. and P. G. Brewer. 1971. Vertical advection diffusion and redox potentials as controls on the distribution of manganese and other trace metals dissolved in waters of the Black Sea. *Journal of Geophysical Research* 76:5877-5891.

Steemann-Nielsen, E., L. Kamp-Nielsen and S. Wium-Anderson. 1969. The effect of deletereous concentrations of copper on the photosynthesis of *Chlorella pyrenoidosa*. *Physiologia Planatarum* 22:1121-1133.

Steemann-Nielsen, E. and S. Wium-Anderson. 1970. Copper ions as poison in the sea and in freshwater. *Marine Biology* 6:93-97.

Steemann-Nielsen, E. and S. Wium-Anderson. 1971. The influence of copper on photosynthesis and growth in diatoms. *Physiologia Plantarum* 24:480-484.

Stumm, W. and H. Balinski. 1973. Trace metals in natural waters; difficulties of interpretation arising from our ignorance on their speciation. In: *Advances in Water Pollution Research*. Sixth International Conference, Jerusalem, June 8-23, 1972. Pergamon, Oxford. pp. 39-49.

Stumm, W. and P. A. Brauner. 1975. Chemical speciation. In: *Chemical Oceanography*, J. P. Riley and G. Skirrow, eds. Academic Press, London Vol. 1, 2nd edition. pp. 173-239.

Stumm, W. W. and J. J. Morgan. 1970. *Aquatic chemistry*. John Wiley and Sons, New York. 583 pp.

Sverdrup, H. V., M. W. Jounson and R. H. Fleming. 1942. *The Ocean*. Prentice Hall, Inc., Englewood Cliffs, N.J. 1087 pp.

Underkofler, W. L. and I. Shain. 1965. Investigation of a.c. polarography at stationary electrodes with application to stripping analysis. *Analytical Chemistry* 37:218-222.

Veeh, H. H. and K. Boström. 1971. Anamolous U^{234}/U^{238} on the East Pacific Rise. *Earth and Planetary Science Letters* 10:372-374.

Vuceta, J. 1976. Adsorption of Pb(11) and Cu(11) on quartz from aqueous solutions: influence of pH, ionic strength and complexing ligands. Ph.D. dissertation. California Institute of Technology. 206 pp.

Wood, J. M. 1973. Metabolic cycles for toxic elements in aqueous systems. Revue Internationale Oceanographic Medicale 31-33:7-16.

Wyrtki, K. The oxgen minima in relation to ocean circulation. *Deep-Sea Research* 9:11-23.

Zeitzschel, B. 1970. Suspended particulate matter in the Gulf of California. *Marine Biology* 7:319-323.

Zirino, A. and M. L. Healy. 1972. pH controlled differential voltammetry of certain trace transition elements in natural waters. *Environmental Science and Technology* 6:243-249.

Zirino, A. and S. Yamamoto. 1972. A pH-dependent model for the chemical speciation of copper, zinc, cadmium and lead in seawater. *Limnology and Oceanography* 17:661-671.

Zittell, H. E. and F. J. Miller. 1965. A glassy-carbon electrode for voltammetry. *Analytical Chemistry* 37:200-203.